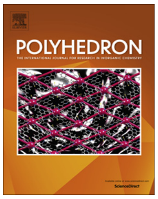
Polyhedron xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly



Partially fluorinated Scorpionate $[HB(3\text{-}(CF_3),5\text{-}(Ph)Pz)_3]^-$ as a supporting ligand for silver(I)-benzene, -carbonyl, and -PPh_3 complexes

Shawn G. Ridlen, Naveen V. Kulkarni, H.V. Rasika Dias *

Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, TX 76019, United States

ARTICLE INFO

Article history:
Received 28 July 2016
Accepted 8 September 2016
Available online xxxx

Keywords:
Silver
Nitrogen ligands
Coordination
X-ray crystallography
NMR spectroscopy

ABSTRACT

The benzene, CO, and PPh_3 adducts $[HB(3\text{-}(CF_3),5\text{-}(Ph)Pz)_3]AgL$ ($L = C_6H_6$, CO, or PPh_3) have been synthesized by a metathesis process using $[HB(3\text{-}(CF_3),5\text{-}(Ph)Pz)_3]Na(THF)$, CF_3SO_3Ag, and the corresponding co-ligands. These silver(I) adducts have been characterized by NMR spectroscopy, and by X-ray crystallography. In all cases the Scorpionate is bound to silver in typical κ^3-fashion. The X-ray crystallographic data of $[HB(3\text{-}(CF_3),5\text{-}(Ph)Pz)_3]Ag(\eta^2\text{-}C_6H_6)$ show that it has a η^2-bound benzene molecule. NMR data point to fluxional behavior in solution. The ^{13}C NMR resonance corresponding to the CO moiety of $[HB(3\text{-}(CF_3),5\text{-}(Ph)Pz)_3]Ag(CO)$ appears as a single peak at δ 177.4 ppm and the $\bar{\nu}_{co}$ is observed at 2148 cm^{-1}. These values indicate the presence of a fairly Lewis acidic silver atom in $[HB(3\text{-}(CF_3),5\text{-}(Ph)Pz)_3]Ag(CO)$ and significantly diminished Ag → CO π-backbonding. Interesting coupling is observed in the solution ^{19}F and ^{31}P NMR spectra of the Ag(I) adduct $[HB(3\text{-}(CF_3),5\text{-}(Ph)Pz)_3]Ag(PPh_3)$. A detailed analysis of the spectral and structural features of these complexes has been described herein.

1. Introduction

Poly(pyrazolyl)borates are a very popular class of ligands in coordination chemistry [1–5]. Since some modes of poly(pyrazolyl)borate ligand–metal ion interactions resemble hunting habits of a scorpion, they are often referred to as Scorpionates [1]. Poly(pyrazolyl)borates are also remarkably versatile group of ligands because, their steric and electronic properties can be modified quite easily by varying the number and type of substituents on the pyrazolyl moieties and on the boron atom. Many Poly(pyrazolyl)borate ligand varieties are known and the majority contain various hydrocarbon substituents (e.g., Me, *i*-Pr, *t*-Bu, Ph, Mesityl) on the pyrazolyl moieties [2,5].

An area of research focus in our laboratory concerns the chemistry of fluorinated poly(pyrazolyl)borates [6–11] and other azolyl analogs like tris(triazolyl)borates [12,13]. For example, we have reported the synthesis of $[HB(3\text{-}(CF_3)Pz)_3]^-$ [8], $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ (Fig. 1) [7,8], $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]^-$ [14], $[HB(3,5\text{-}(CF_3)_2,4\text{-}(Cl)Pz)_3]^-$ [15], $[HB(3,5\text{-}(CF_3)_2,4\text{-}(NO_2)Pz)_3]^-$ [15], $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]^-$ [9], as well as the B-alkylated and B-arylated systems like $[MeB(3\text{-}(CF_3)Pz)_3]^-$ and $[PhB(3\text{-}(CF_3)Pz)_3]^-$ [16,17]. Scorpionates bearing longer fluoroalkyl substituents on the pyrazolyl moieties are also known [18–20].

Ligands such as $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ have electron withdrawing fluoroalkyl groups and are significantly less electron-rich and weaker donors compared to the non-fluorinated systems like $[HB(3,5\text{-}(CH_3)_2Pz)_3]^-$ [21]. Metal adducts of fluorinated tris(pyrazolyl)borates therefore possess more electrophilic metal sites. They display greater catalytic activity in certain reactions like in the C–H and C–halogen bond functionalization chemistry via carbene insertion, compared to the non-fluorinated, electron rich tris(pyrazolyl)borate analogs [15,22–29]. Fluorinated Scorpionates like $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ and $[HB(3\text{-}(CF_3),5\text{-}(CH_3)Pz)_3]^-$ are also of interest because perfluoroalkyl groups at the pyrazolyl moiety 3-positions provide a robust environment around the metal site. The C–F bonds are strong and less prone to intramolecular activation (compared for example, to C–H bonds) when reactive species are generated at the metal site. Fluorinated tris(pyrazolyl)borates are useful as effective supporting ligands in metal mediated oxidation chemistry [30–33]. Other fluorinated Scorpionates and Scorpionates bearing other types of electron withdrawing substituents such as nitro groups, cyanides, and halogens have been reported as well [34–49].

In this paper, we describe the successful use of a mixed aryl-perfluoroalkyl substituent bearing tris(pyrazolyl)borate ligand in silver chemistry. In particular, we report the synthesis and complete characterization of Ag(I)-benzene, Ag(I)-carbonyl,

---

* Corresponding author.
E-mail address: dias@uta.edu (H.V.R. Dias).
URL: https://www.uta.edu/chemistry/faculty/directory/Dias.php (H.V.R. Dias).

http://dx.doi.org/10.1016/j.poly.2016.09.014
0277-5387/

Please cite this article in press as: S.G. Ridlen et al., Polyhedron (2016), http://dx.doi.org/10.1016/j.poly.2016.09.014

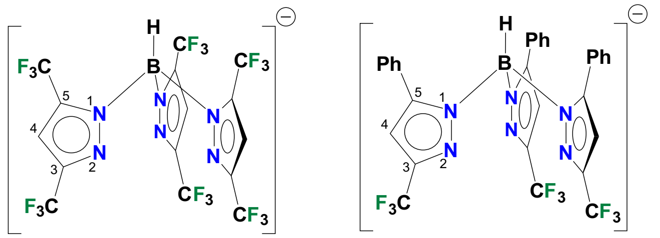


Fig. 1. Fluorinated tris(pyrazolyl)borate ligands $[HB(3,5-(CF_3)_2Pz)_3]^-$ and $[HB(3-(CF_3),5-(Ph)Pz)_3]^-$.

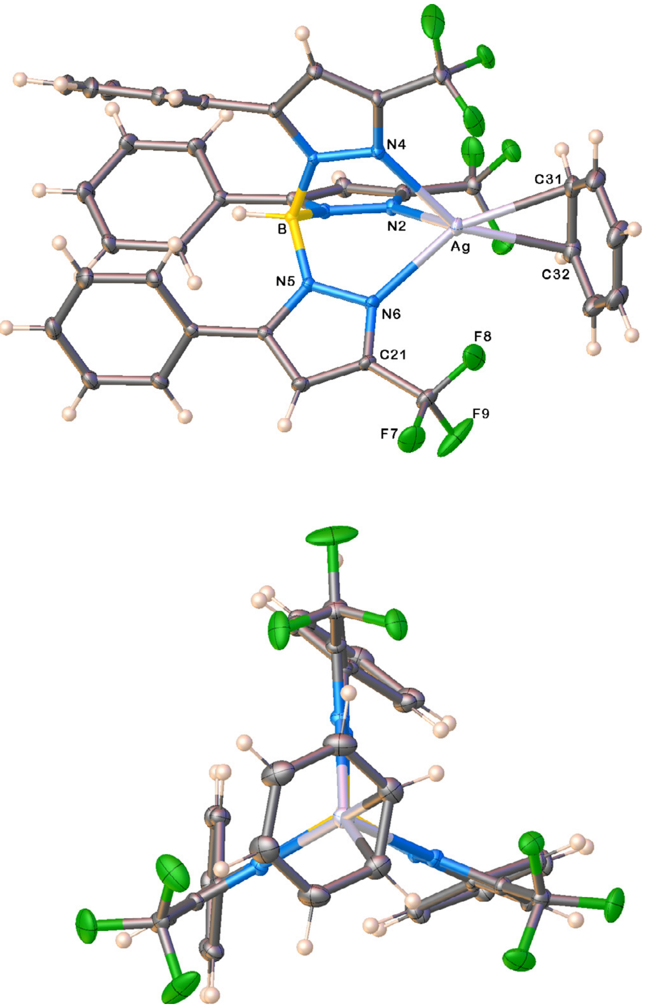


Fig. 2. Top: ORTEP diagram of $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(\eta^2-C_6H_6)$ (thermal ellipsoids set at 50% probability). Selected bond distances (Å) and angles (°): Ag–N2 2.4170(9), Ag–N4 2.3505(9), Ag–N6 2.3463(9), Ag–C31 2.4507(12), Ag–C32 2.4480 (12), Ag···(C31–C32 centroid) 2.347, Ag···B 3.343; N4–Ag–N2 80.61(3), N4–Ag–N6 81.56(3), N2–Ag–N6 84.41(3), C31–Ag–C32 33.29(4), B···Ag···(C31–C32 centroid) 161.3. Bottom: A view down Ag···B axis.

and Ag(I)-PPh_3 adducts supported by $[HB(3-(CF_3),5-(Ph)Pz)_3]^-$. Isolation of silver(I) Scorpionates is challenging because they have a tendency to decompose thermally or photochemically producing metallic silver, especially when reducing borohydride moieties are present on the supporting ligand backbone.

2. Results and discussion

The Scorpionate precursor $[HB(3-(CF_3),5-(Ph)Pz)_3]Na(THF)$ used in this work has been reported previously [50]. The silver(I)-benzene complex $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(\eta^2-C_6H_6)$ was obtained by treating $[HB(3-(CF_3),5-(Ph)Pz)_3]Na(THF)$ with CF_3SO_3Ag in a dichloromethane-benzene solvent mixture. It is a white solid, and forms very good quality colorless crystals with well-defined faces.

X-ray crystallographic data of $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(\eta^2-C_6H_6)$ show that is has a η^2-bound benzene molecule (Fig. 2). The Ag–C31 and Ag–C32 distances are equal. The benzene molecule is tilted relative to the Scorpionate face, and the angle between Ag–C31–C32 plane and benzene ring plane is about 102°. The silver atom adopts a distorted tetrahedral geometry, with the Scorpionate showing κ^3-coordination mode. There are no reports of structurally characterized silver Scorpionates with benzene co-ligands for comparison [51]. However, related toluene complexes $[HB(3,5-(CF_3)_2Pz)_3]Ag(\eta^2\text{-toluene})$ and $[HB(3-(CF_3),5-(CH_3)Pz)_3]Ag(\eta^2\text{-toluene})$ are known and they also have η^2-bound arenes [52,53]. Interestingly, in contrast to $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(\eta^2-C_6H_6)$, the silver-arene bonding in $[HB(3,5-(CF_3)_2Pz)_3]Ag(\eta^2\text{-toluene})$ which has a very weakly donating Scorpionate, is rather asymmetric with significantly different Ag–C distances (range 2.414–2.505 Å for two molecules in the asymmetric unit). The average Ag–C distances however, do not show a large difference (e.g., av. Ag–C of 2.449, 2.425, 2.448 Å for $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(\eta^2-C_6H_6)$, $[HB(3-(CF_3),5-(CH_3)Pz)_3]Ag(\eta^2\text{-toluene})$ and $[HB(3,5-(CF_3)_2Pz)_3]Ag(\eta^2\text{-toluene})$, respectively). Average Ag–N distances also do not show a major variation (2.371, 2.367, and 2.390 Å, respectively, for the three adducts listed above with the highest value not unexpectedly associated with the more weakly donating Scorpionate).

The solution NMR spectra of $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(\eta^2-C_6H_6)$ in CD_2Cl_2 at room temperature show only one sharp proton and one carbon signal for the benzene moiety, and one fluorine signal for the Scorpionate. This indicates the presence of a fluxional benzene ligand. The ^1H resonance of C_6H_6 in $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(\eta^2-C_6H_6)$ (δ 7.42 ppm) shows a small down-field shift compared to the corresponding peak of free benzene in the same solvent (δ 7.35 ppm) [54].

The silver (I) carbonyl adduct $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(CO)$ was synthesized by treating a mixture of $[HB(3-(CF_3),5-(Ph)Pz)_3]Na(THF)$ [50] and CF_3SO_3Ag in dichloromethane with carbon monoxide (1 atm). It is a white solid. The characteristic $\bar{\nu}_{co}$ band of $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(CO)$ can be observed at 2148 cm^{-1} in the IR spectrum, which is higher than the $\bar{\nu}_{co}$ of the free CO (2143 cm^{-1}). This is indicative of a significantly high electrostatic component in the Ag–CO interaction and diminished Ag → CO π-backbonding, which is not surprising since the silver(I) atom supported by the fluorinated $[HB(3-(CF_3),5-(Ph)Pz)_3]^-$ is expected to be fairly electrophilic [50]. A comparison of $\bar{\nu}_{co}$ values to silver carbonyl adducts supported by more weakly and strongly donating Scorpionates $[HB(3,5-(CF_3)_2Pz)_3]Ag(CO)$ and $[MeB(3-(Mes)Pz)_3]Ag(CO)$ show that the CO stretch of $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(CO)$ is in the expected range (Table 1). We have also observed the ^{13}C NMR resonance corresponding to the CO moiety of $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(CO)$. It appears as a singlet at δ 177.4 ppm in CD_2Cl_2 at room temperature. The absence of $^{107/109}Ag-^{13}C$ coupling in solution probably an indication for the presence of a labile CO ligand in $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(CO)$ that dissociates-coordinates rapidly in CD_2Cl_2 on the NMR timescale. For comparison, the corresponding signals of $[HB(3,5-(CF_3)_2Pz)_3]Ag(CO)$ and free CO were reported at δ 175.5 and 184 ppm, respectively. Based on these IR and NMR data, $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(CO)$ can be considered as a non-classical metal carbonyl adduct [55]. The classical metal carbonyls like $Cr(CO)_6$ with significant metal → CO π-backbonding, in contrast, show low CO stretching frequencies (e.g., 2000 cm^{-1}) [56] and higher ^{13}C NMR chemical shifts (e.g., δ

Please cite this article in press as: S.G. Ridlen et al., Polyhedron (2016), http://dx.doi.org/10.1016/j.poly.2016.09.014

Table 1
Selected spectroscopic and structural data for tris(pyrazolyl)boratosilver(I) carbonyls.

Scorpionate	δ (^{13}CO) (NMR, ppm)	$\bar{\nu}$ (CO) (IR, cm^{-1})	Ag–C (Å)	Ref.
$[HB(3\text{-}(CF_3),5\text{-}(Ph)Pz)_3]^-$	177.4 (CD_2Cl_2)	2148 (neat)	2.019(2)	This work
$[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$	175.5 (CD_2Cl_2)	2178 (Nujol)	2.037(5)	[52]
$[HB(3,4,5\text{-}(CF_3)_3Pz)_3]^-$		2177 (KBr)	2.083(3)	[14]
$[HB(3,5\text{-}(CF_3)_2,4\text{-}BrPz)_3]^-$		2167 (soln.)		[58]
$[HB(3,4,5\text{-}(Br)_3Pz)_3]^-$		2153 (THF)		[37]
$[MeB(3\text{-}(C_2F_5)Pz)_3]^-$	176.1 ($CDCl_3$)	2153 (KBr)	2.030(4)	[19]
$[MeB(3\text{-}(CF_3)Pz)_3]^-$		2152 (hexane)		[25]
$[MeB(3\text{-}(Mes)Pz)_3]^-$		2128 (hexane)	1.994(3)	[59]
Free CO	*184*	*2143*		[6,55]

212.3 ppm) [57], relative to the corresponding values for the free CO.

The treatment of $[HB(3\text{-}(CF_3),5\text{-}(Ph)Pz)_3]Ag(CO)$ with excess benzene in dichloromethane led to the loss of CO and the formation of $[HB(3\text{-}(CF_3),5\text{-}(Ph)Pz)_3]Ag(\eta^2\text{-}C_6H_6)$. It is also possible to regenerate $[HB(3\text{-}(CF_3),5\text{-}(Ph)Pz)_3]Ag(CO)$ from $[HB(3\text{-}(CF_3),5\text{-}(Ph)Pz)_3]Ag(\eta^2\text{-}C_6H_6)$ by exposing it to CO in dichloromethane. This suggest the presence of rather labile CO and benzene co-ligands in these two silver Scorpionate adducts.

X-ray crystal structure of $[HB(3\text{-}(CF_3),5\text{-}(Ph)Pz)_3]Ag(CO)$ shows that it features a κ^3-bonded tris(pyrazolyl)borate and a pseudo-tetrahedral silver site (Fig. 3). The Ag–CO moiety is essentially linear. Isolable silver(I) adducts are rare. Search of Cambridge Structural Database show that there are only four structurally characterized tris(pyrazolyl)boratosilver(I) carbonyl complexes in the literature. Some of their structural and spectroscopic features are summarized in Table 1 with several other related adducts observed spectroscopically. The Ag–C bond distances of these adducts range from 2.083(3) to 1.994(3) Å. The corresponding distance of 2.019(2) Å observed for the $[HB(3\text{-}(CF_3),5\text{-}(Ph)Pz)_3]Ag(CO)$ lies closer to the shorter end of the spectrum. For comparison, the copper(I) analog $[HB(3\text{-}(CF_3),5\text{-}(Ph)Pz)_3]Cu(CO)$ [50] is known and it has a much shorter Cu–C distance (1.773(5) Å), consistent with the smaller atomic radius of copper [60–62]. The characteristic $\bar{\nu}_{co}$ band of the copper analog appears at 2103 cm^{-1} in the IR spectrum, which is lower than the $\bar{\nu}_{co}$ of free CO [50].

The reaction between $[HB(3\text{-}(CF_3),5\text{-}(Ph)Pz)_3]Na(THF)$ and CF_3SO_3Ag in the presence of PPh_3 afforded $[HB(3\text{-}(CF_3),5\text{-}(Ph)Pz)_3]Ag(PPh_3)$, which was isolated as a white solid in 80% yield. It was characterized by ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectroscopy. The ^{19}F and ^{31}P NMR spectra are the most interesting as they not only show coupling to each other but also to spin active silver nuclei ($I = ½$; ^{109}Ag (48.2%) and ^{107}Ag (51.8%)). For example, the ^{19}F resonance corresponding to the CF_3 groups at pyrazolyl moiety 3-positions appear as a doublet of doublet at δ −60.27 ppm due to coupling to ^{31}P and $^{107/109}$Ag nuclei (Fig. 4). For comparison, the corresponding signal in $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(PPh_3)$ also appears as a doublet of doublet, whereas in the copper adduct $[HB(3,5\text{-}(CF_3)_2Pz)_3]Cu(PPh_3)$, it shows up as a doublet [8]. The ^{31}P NMR spectrum of $[HB(3\text{-}(CF_3),5\text{-}(Ph)Pz)_3]Ag(PPh_3)$ is equally informative as the phosphorus signal of silver bound PPh_3 appears as a doublet of doublet of multiplet centered at δ 17.8 ppm (Fig. 4). The coupling of ^{31}P to the two silver isotopes is well resolved with $^1J(^{31}P\text{-}^{107}Ag) = 634$ Hz and $^1J(^{31}P,^{109}Ag) = 732$ Hz. The $^1J(^{31}P,^{109}Ag)/^1J(^{31}P\text{-}^{107}Ag)$ ratio is consistent with the $^{109}Ag/^{107}Ag$ gyromagnetic ratio of 1.149. The magnitude of $^1J(Ag\text{–}P)$ coupling is at the higher end of four-coordinate silver phosphine complexes [63]. Each of these signals also shows spin–spin coupling to nine fluorine atoms of the CF_3 groups. Such long range coupling has been observed in the ^{31}P NMR spectra of

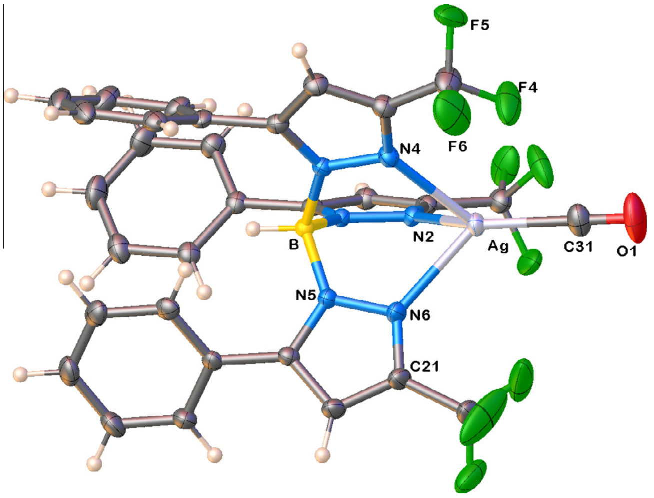


Fig. 3. Top: ORTEP diagram of $[HB(3\text{-}(CF_3),5\text{-}(Ph)Pz)_3]Ag(CO)$ (thermal ellipsoids set at 50% probability). Selected bond distances (Å) and angles (°): Ag–N2 2.2931(18), Ag–N4 2.3197(18), Ag–N6 2.3051(18), Ag–C31 2.019(2), O1–C31 1.110(3), Ag···B 3.317; N4-Ag–N2 85.13(6), N4-Ag–N6 82.74(6), N2-Ag–N6 80.34(6), O1–C31–Ag 177.1(3), B···Ag–C31 176.5.

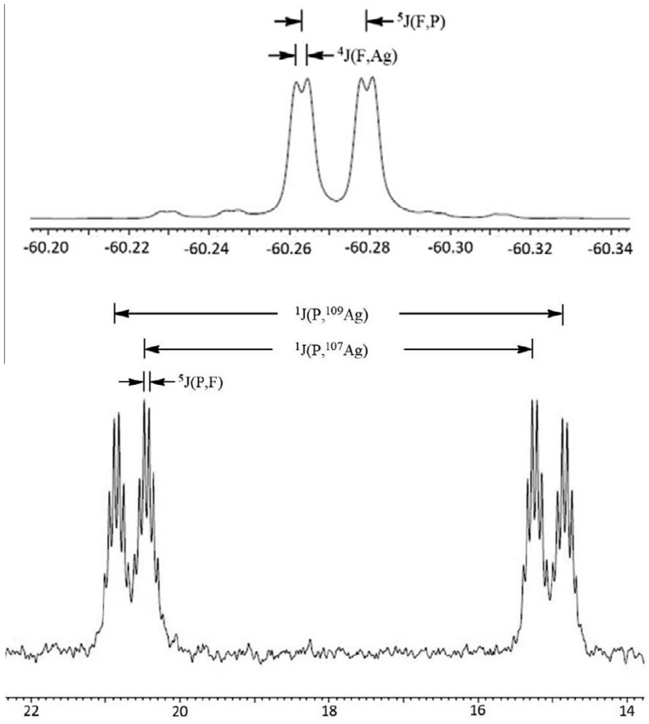


Fig. 4. Top: ^{19}F NMR spectrum of $[HB(3\text{-}(CF_3),5\text{-}(Ph)Pz)_3]Ag(PPh_3)$, **Bottom:** $^{31}P\{^1H\}$ NMR spectrum of $[HB(3\text{-}(CF_3),5\text{-}(Ph)Pz)_3]Ag(PPh_3)$.

Please cite this article in press as: S.G. Ridlen et al., Polyhedron (2016), http://dx.doi.org/10.1016/j.poly.2016.09.014

$[HB(3,5-(CF_3)_2Pz)_3]Ag(PPh_3)$ and $[HB(3-(CF_3),5-(CH_3)Pz)_3]Ag(PPh_3)$ adducts [64–66]. The well resolved coupling in $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(PPh_3)$ points to the lack of Scorpionate and PPh_3 ligand dissociation on the NMR timescale.

Although further studies are needed to ascertain whether these “long-range” $^5J(P–F)$ couplings are a result of through-bond or through-space interaction between phosphorous and fluorine spins, we note that the closest nonbonded intramolecular P···F distance in crystalline $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(PPh_3)$ is short at 3.62 Å, and may be close enough to permit through-space, Fermi-contact spin–spin coupling by the interaction between phosphorus with fluorines of the CF_3 groups. In fact, the closest separation in solution would be even less and estimated to be about 3.2–3.3 Å (which is near the sum of the P and F van der Waals radii of 3.27 or 3.36 Å according to Bondi or Alvarez) [67], because in the crystal structure, Ag and P atoms lie on a plane which dissects the F-C-F angle of CF_3 groups. It is also noteworthy that very large (>800 Hz), long-range Tl–F coupling has been reported in fluorinated Scorpionate complexes of thallium such as $[HB(3-(CF_3),5-(2\text{-thienyl})Pz)_3]Tl$ and $[MeB(3-(CF_3)Pz)_3]Tl$ [16,44].

The X-ray crystal structure of $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(PPh_3)$ is illustrated in Fig. 5. The Scorpionate is bonded to the silver atom in a typical κ^3-fashion. The Ag–P and average Ag–N bond distances are within the normal range observed for silver-Scorpionates with phosphine co-ligands (Table 2). In general, they are closer in value to the corresponding distances reported for $[HB(3-(CF_3),5-(CH_3)Pz)_3]Ag(PPh_3)$.

Solid samples of C_6H_6, CO, and PPh_3 adducts $[HB(3-(CF_3),5-(Ph)Pz)_3]AgL$ (L = C_6H_6, CO, or PPh_3) can be exposed to air and indoor lighting at room temperature for several minutes without obvious signs of decomposition and do not lose co-ligands under reduced pressure. Although they are moderately air stable, these complexes should be kept under nitrogen and protected from light for long term storage. The complex $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(PPh_3)$ shows excellent solution stability and does not decompose after being exposed to air and ambient light for several days. Conversely, $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(C_6H_6)$ and $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(CO)$ slowly form black precipitates over several hours when dissolved in chlorinated solvents, even when protected from exposure to air and indoor lighting.

3. Conclusions

In summary, we have reported the isolation and characterization of three new silver(I) complexes supported by $[HB(3-(CF_3),5-(Ph)Pz)_3]^-$ ligand. The benzene and carbonyl adducts of silver Scorpionates are particularly rare. $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(\eta^2-C_6H_6)$ has an η^2-bound benzene on silver(I). The $\bar{\nu}_{co}$ of $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(CO)$ appear at 2148 cm^{-1} and can be considered as a non-classical metal carbonyl complex. The phosphine adduct $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(PPh_3)$ shows interesting ^{19}F and ^{31}P NMR spectra with coupling to each other and spin active silver. Silver Scorpionates supported by weakly coordinating ligands are useful in catalysis and are good ligand transfer agents. We are currently exploring the coordination chemistry of $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag$ with various other co-ligands.

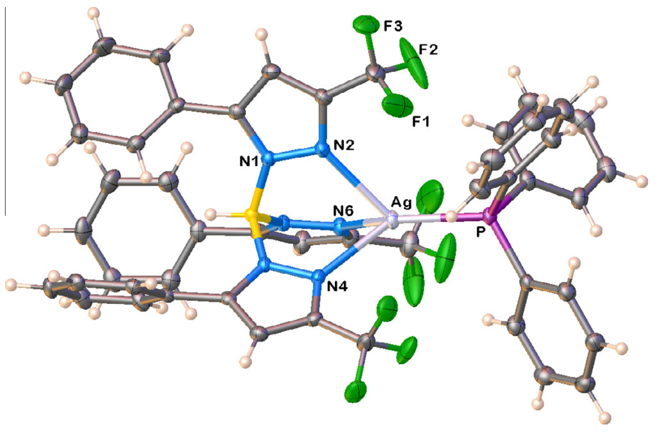


Fig. 5. Top: ORTEP diagram of $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(PPh_3)$ (thermal ellipsoids set at 50% probability). Selected bond distances (Å) and angles (°): Ag–P 2.3690(7), Ag–N2 2.410(2), Ag–N4 2.349(2), Ag–N6 2.415(2), P-C31 1.831(3), P-C37 1.831(3), P-C43 1.830(3), Ag···B 3.420; N4–Ag–N2 80.43(7), N4–Ag–N6 79.56(7), N2–Ag–N6 80.40(7), B···Ag–P 176.1.

4. Experimental

4.1. General

All manipulations were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques or in a Vacuum Atmosphere single-station glovebox equipped with a −25 °C refrigerator. Solvents were purchased from commercial sources and purified prior to use. Glassware was oven-dried at 150 °C overnight. NMR spectra were recorded at 25 °C on JEOL Eclipse 500 (^1H, 500.16 MHz; ^{13}C, 125.77 MHz; ^{19}F, 470.62 MHz; and ^{31}P, 121.66 MHz) or JEOL Eclipse 300 spectrometers. Proton and carbon chemical shifts are referenced using the residual proton or carbon signals of the deuterated solvent. ^{19}F NMR values were referenced to external $CFCl_3$, and ^{31}P NMR values were referenced to external H_3PO_4 (85%). Melting points were obtained on a Mel-Temp II apparatus. Elemental analyses were performed at Intertek Pharmaceutical Services. IR spectra were collected at room temperature on a Shimadzu IRPrestige-21 FTIR containing an ATR attachment. Silver(I) trifluoromethanesulfonate (CF_3SO_3Ag) and triphenyl phosphine (PPh_3) were purchased from Sigma–Aldrich and carbon monoxide gas was purchased from Airgas. $[HB(3-(CF_3),5-(Ph)Pz)_3]Na(THF)$ [50] was prepared via a reported procedure.

4.2. $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(\eta^2-C_6H_6)$

$[HB(3-(CF_3),5-(Ph)Pz)_3]Na(THF)$ (0.25 g, 0.34 mmol) and CF_3SO_3Ag (0.095 g, 0.37 mmol) were placed in a Schlenk flask under nitrogen atmosphere and the flask was covered aluminum foil to protect it from light. Dichloromethane (20 mL) and benzene (2.0 mL) were combined in a separate Schlenk flask and slowly added via syringe. The resulting solution was stirred overnight at room temperature and filtered through a bed of Celite to remove the insoluble material. The filtrate was concentrated under reduced pressure and placed in a freezer maintained at −20 °C. X-ray quality crystals of $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(\eta^2-C_6H_6)$ were obtained after several days at −20 °C. Yield: 0.234 g, 83%; m.p. 83–120 °C (slowly decomposes over this wide temperature range with a final melting point of the residue at 211 °C). ^1H NMR (CD_2Cl_2, 500.16 MHz, 298 K) δ (ppm): 7.42 (s, 6H, C_6H_6), 7.23 (t, 3H, Ph-H, $^3J_{HH}$ = 7.25 Hz), 6.95 (t, 6H, Ph-H, $^3J_{HH}$ = 8.00 Hz), 6.90 (d, 6H, Ph-H, $^3J_{HH}$ = 6.6 Hz), 6.57 (s, 3H, Pz-CH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.77 MHz, 298 K) δ (ppm): 152.2 (s, $C(C_6H_5)$), 143.0 (q, $^2J(C,F)$ = 37 Hz, CCF_3), 131.6 (s, Ph), 130.2 (s, Ph), 128.5 (s, Ph), 128.5 (s, C_6H_6), 128.2 (s, Ph), 121.1 (q, $^1J(C,F)$ = 269 Hz, CF_3), 105.0 (s, CH). ^{19}F NMR (CD_2Cl_2, 470.62 MHz, 298 K) δ(ppm): −61.98 (s, 9F). ATR-FTIR (Selected peak, cm^{-1}): $\bar{\nu}$ = 2628 (B-H). *Anal.* Calc. for $C_{36}H_{25}AgBF_9N_6{\cdot}0.5CH_2Cl_2$: C, 50.17; H, 3.00; N, 9.62. Found. C, 50.38; H, 2.99; N, 9.86%.

Please cite this article in press as: S.G. Ridlen et al., Polyhedron (2016), http://dx.doi.org/10.1016/j.poly.2016.09.014

Table 2
Selected spectroscopic and structural data for tris(pyrazolyl)boratosilver(I) PPh_3 complexes.

Scorpionate	δ (^{31}P) (NMR, ppm)[a]	Ag–P (Å)	Average Ag–N (Å)	$^1J(^{31}P-^{107}Ag)$	$^1J(^{31}P-^{109}Ag)$	Ref.
$[HB(3-(CF_3),5-(Ph)Pz)_3]^-$	17.9 (C_6D_6)	2.3690(7)	2.391	633.9	732.4	This work
$[HB(3-(CF_3),5-(CH_3)Pz)_3]^-$	16.53 ($CDCl_3$)	2.3642(5)	2.386	631.8	729.0	[53]
$[HB(3,5-(CF_3)_2Pz)_3]^-$	17.8 (C_6D_6)	2.376(1)	2.432	657.5	758.8	[8]
$[HB(3,5-(CH_3)_2Pz)_3]^-$	17.9 ($CDCl_3$)	2.347(6)	2.345	576	665	[63,68]
$[HB(4-BrPz)_3]^-$	16.9 ($CDCl_3$)	2.345(3)	2.374	613	707	[63]
$[HB(Pz)_3]^-$	17.0 ($CDCl_3$)	2.337(3)	2.341	607	700	[63]
$[HB(3,5-(Ph)_2Pz)_3]^-$	13.4 ($CDCl_3$)	2.360(1)	2.370	600	693	[69]
$[HB\{3,5-(Me),4-(C_5H_4N)Pz\}_3]^-$	18.2 ($CDCl_3$)	2.3403(6)	2.338	584	675	[70]
[a]*Free* PPh_3	*−6.0*					*[71]*

Table 3
Crystal Data and Summary of Data Collection and Refinement for $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(\eta^2-C_6H_6)$, $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(CO)\cdot CH_2Cl_2$ and $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(PPh_3)$.

Compound	$[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(\eta^2-C_6H_6)$	$[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(CO)\cdot CH_2Cl_2$	$[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(PPh_3)$
Empirical formula	$C_{36}H_{25}AgBF_9N_6$	$C_{32}H_{21}AgBCl_2F_9N_6O$	$C_{48}H_{34}AgBF_9N_6P$
Formula weight	831.30	866.13	1015.46
T (K)	100.01	99.99	106.78
λ (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/n$	$Pbcn$	$P2_1/n$
Unit-cell dimensions	a = 13.3013(5) Å	a = 23.8118(17) Å	a = 13.1909(9) Å
	b = 12.7215(4) Å	b = 16.7916(12) Å	b = 18.2128(12) Å
	c = 20.7889(7) Å	c = 17.0571(12) Å	c = 18.3172(12) Å
	α = 90°	α = 90°	α = 90°
	β = 104.6960(10)°	β = 90°	β = 94.006(2)°
	γ = 90°	γ = 90°	γ = 90°
V (Å^3)	3402.7(2)	6820.1(8)	4389.8(5)
Z	4	8	4
D_{cal} (Mg m^{-3})	1.623	1.687	1.536
Absorption coefficient (mm^{-1})	0.679	0.835	0.577
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0316, wR_2 = 0.0644	R_1 = 0.0322, wR_2 = 0.0759	R_1 = 0.0343, wR_2 = 0.0824
R indices (all data)	R_1 = 0.0473, wR_2 = 0.0689	R_1 = 0.0392, wR_2 = 0.0805	R_1 = 0.0455, wR_2 = 0.0929

4.3. $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(CO)$

$[HB(3-(CF_3),5-(Ph)Pz)_3]Na(THF)$ (0.25 g, 0.34 mmol) and CF_3SO_3Ag (0.087 g, 0.34 mmol) were placed in a Schlenk flask under a nitrogen atmosphere and the flask was covered aluminum foil to protect it from light. An atmosphere of CO was established and dichloromethane (25 mL) was added to the flask. The resulting mixture was stirred at RT for 1 h while gently bubbling CO, to obtain a solution with some black precipitate. It was filtered through a bed of Celite to obtain a clear colorless solution. The solution was concentrated by bubbling CO and placed in a freezer maintained at −20 °C overnight under a positive pressure of CO to obtain X-ray quality colorless crystals. Yield 0.197 g, 75%; m.p. 106–192 °C (slowly decomposes over this wide temperature range and finally melts 192 °C). ^1H NMR (CD_2Cl_2, 500.16 MHz, 298 K) δ (ppm): 7.24 (t, 3H, Ph), 6.90 (m, 12H, Ph), 6.56 (s, 3H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.77 MHz, 298 K) δ (ppm): 177.4 (s, *C*O), 151.2 (s, $C(C_6H_5)$), 143.2 (q, $^2J(C,F)$ = 36 Hz, CCF_3), 131.2 (s, Ph), 130.2 (s, Ph), 128.9 (s, Ph), 128.3 (s, Ph), 121.9 (q, $^1J(C,F)$ = 269 Hz, CF_3), 105.0 (s, *C*H). ^{19}F NMR (CD_2Cl_2, 470.62 MHz, 298 K) δ (ppm): −61.68 (s, 9F). ATR-FTIR (Selected peak, cm^{-1}): $\bar{\nu}$ = 2629 (B-H), 2148 (CO). *Anal.* Calc. for $C_{31}H_{19}AgBF_9N_6O$: C, 47.66; H, 2.45; N, 10.76. Found. C, 47.27; H, 2.07; N, 10.67%.

4.4. $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(PPh_3)$

$[HB(3-(CF_3),5-(Ph)Pz)_3]Na(THF)$ (0.25 g, 0.34 mmol) and PPh_3 (0.089 g, 0.34 mmol) were dissolved in THF (10 mL) and this mixture was slowly added to a stirring solution of CF_3SO_3Ag (0.087 g, 0.33 mmol) in THF (10 mL) at 0 °C under an atmosphere of nitrogen. The flask was covered aluminum foil to protect it from light. After 1 h, the solution was allowed to warm to room temperature and stirred for additional 30 min. The reaction solvent was removed under vacuum, and the residue was extracted into toluene. The resulting mixture was filtered through bed of Celite and the solvent was removed under reduced pressure to obtain a white solid, which was thoroughly washed with hexanes and dried under vacuum. X-ray quality crystals were obtained from a dichloromethane solution stored at −20 °C. Yield: 0.274 g, 80%; m.p. 96–154 °C (slowly decomposes over this wide temperature range with a final melting point of the residue at 224 °C). ^1H NMR (C_6D_6, 500.16 MHz, 298 K) δ (ppm): 7.89 (m, 6H, Ph), 7.18, (m, 12H, Ph), 7.12 (m, 3H, Ph), 6.99 (m, 3H, Ph), 6.78 (m, 12H, Ph), 6.34 (s, 3H, Pz-C*H*). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.77 MHz, 298 K) δ (ppm): 151.8 (s, *C*Ph), 144.1 (q, $^2J(C,F)$ = 36 Hz, CCF_3), 135.0 (d, $^2J(C,P)$ = 17 Hz, PPh_3), 133.3 (dd, ^1J = 34, ^2J = 5 Hz, PPh_3), 132.2 (s, PPh_3), 130.9 (s, Ph), 130.5 (s, Ph), 129.3 (d, $^3J(C,P)$ = 11 Hz, PPh_3), 122.4 (q, $^1J(C,F)$ = 268 Hz, CF_3), 105.8 (s, *C*H). ^{19}F NMR (C_6D_6, 470.62 MHz, 298 K) δ (ppm): −60.27 (dd, $^5J(F,P)$ = 7.8 Hz, $^4J(F,Ag)$ = 1.3 Hz. $^{31}P\{^1H\}$ NMR (C_6D_6, 121.65 MHz, 298 K) δ (ppm): 17.8 ($^1J(P,^{107}Ag)$ = 633.9 Hz, $^1J(P,^{109}Ag)$ = 732.4 Hz, $^5J(F,P)$ = 7.6 Hz). ATR-FTIR (Selected peak, cm^{-1}): $\bar{\nu}$ = 2623 (B-H). *Anal.* Calc. for $C_{48}H_{34}AgBF_9N_6P$: C, 56.77; H, 3.37; N, 8.28. Found. C, 56.12; H, 3.30; N, 8.25%.

5. X-ray crystallographic data

A suitable crystal covered with a layer of hydrocarbon/paratone-N oil was selected and mounted on a Cryo-loop, and immediately placed in the low temperature nitrogen stream. The X-ray intensity data for $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(C_6H_6)$, $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(CO)$ and $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(PPh_3)$ were

Please cite this article in press as: S.G. Ridlen et al., Polyhedron (2016), http://dx.doi.org/10.1016/j.poly.2016.09.014

measured at 100(2) K or at 106(2) K on a Bruker D8 Quest with a Photon 100 CMOS detector equipped with an Oxford Cryosystems 700 series cooler, a Triumph monochromator, and a Mo Kα fine-focus sealed tube ($\lambda = 0.71073$ Å). Intensity data were processed using the Bruker ApexII program suite. All the calculations for the structure determination were carried out using the SHELXTL package (version 6.14). Initial atomic positions were located by direct methods using XS, and the structures of the compounds were refined by the least-squares method using SHELXL [72]. Absorption corrections were applied by using SADABS. All the non-hydrogen atoms were refined anisotropically. X-ray structural figures were generated using Olex2 [73]. The hydrogen atom on boron and hydrogen atoms of benzene carbons (C31 and C32) bonded to silver in $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(C_6H_6)$ were located in a Fourier difference synthesis and refined satisfactorily. All the remaining hydrogen atoms of $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(C_6H_6)$ as well as hydrogens of $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(CO)$ and $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(PPh_3)$ were placed at calculated positions and refined using a riding model. $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(CO)$ crystallizes with a molecule of CH_2Cl_2 in the asymmetric unit. The fluorine atoms of one CF_3 group in $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(CO)$ and the CH_2Cl_2 show positional disorder over two sites, but these disorders were modeled satisfactorily. Further details are given in Table 3.

Acknowledgments

This work was supported by the National Science Foundation (CHE-01265807) and the Robert A. Welch Foundation (Grant Y-1289).

Appendix A. Supplementary data

CCDC 1495609, 1495610, 1495611 contain the supplementary crystallographic data for $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(C_6H_6)$, $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(CO)$ and $[HB(3-(CF_3),5-(Ph)Pz)_3]Ag(PPh_3)$, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2016.09.014.

References

[1] S. Trofimenko, Chem. Rev. 93 (1993) 943.
[2] S. Trofimenko, Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands, Imperial College, London, 1999.
[3] C. Pettinari, C. Santini, Comp. Coord. Chem. II (1) (2004) 159.
[4] C. Santini, M. Pellei, G.G. Lobbia, G. Papini, Mini-Rev. Org. Chem. 7 (2010) 84.
[5] C. Pettinari, Scorpionates II: Chelating Borate Ligands, Imperial College Press, London, 2008.
[6] H.V.R. Dias, C.J. Lovely, Chem. Rev. 108 (2008) 3223.
[7] H.V.R. Dias, H.-L. Lu, R.E. Ratcliff, S.G. Bott, Inorg. Chem. 34 (1995) 1975.
[8] H.V.R. Dias, W. Jin, H.-J. Kim, H.-L. Lu, Inorg. Chem. 35 (1996) 2317.
[9] H.V.R. Dias, J.D. Gorden, Inorg. Chem. 35 (1996) 318.
[10] H.V.R. Dias, G. Gioia Lobbia, G. Papini, M. Pellei, C. Santini, Eur. J. Inorg. Chem. (2009) 3935.
[11] H.V.R. Dias, S. Alidori, G.G. Lobbia, G. Papini, M. Pellei, C. Santini, Inorg. Chem. 46 (2007) 9708.
[12] X. Kou, J. Wu, T.R. Cundari, H.V.R. Dias, Dalton Trans. (2009) 915.
[13] X. Kou, H.V.R. Dias, Dalton Trans. (2009) 7529.
[14] N.B. Jayaratna, I.I. Gerus, R.V. Mironets, P.K. Mykhailiuk, M. Yousufuddin, H.V.R. Dias, Inorg. Chem. 52 (2013) 1691.
[15] N.B. Jayaratna, D.B. Pardue, S. Ray, M. Yousufuddin, K.G. Thakur, T.R. Cundari, H.V.R. Dias, Dalton Trans. 42 (2013) 15399.
[16] H.V.R. Dias, X. Wang, H.V.K. Diyabalanage, Inorg. Chem. 44 (2005) 7322.
[17] H.V.R. Dias, J. Wu, X. Wang, K. Rangan, Inorg. Chem. 46 (2007) 1960.
[18] H.V.R. Dias, H.-J. Kim, Organometallics 15 (1996) 5374.
[19] H.V.R. Dias, X. Wang, Dalton Trans. (2005) 2985, and the references therein.
[20] H.V.R. Dias, J. Wu, Organometallics 31 (2012) 1511.
[21] H.V.R. Dias, H.-J. Kim, H.-L. Lu, K. Rajeshwar, N.R. de Tacconi, A. Derecskei-Kovacs, D.S. Marynick, Organometallics 15 (1996) 2994.
[22] H.V.R. Dias, R.G. Browning, S.A. Richey, C.J. Lovely, Organometallics 24 (2005) 5784.
[23] H.V.R. Dias, R.G. Browning, S.A. Richey, C.J. Lovely, Organometallics 23 (2004) 1200.
[24] H.V.R. Dias, R.G. Browning, S.A. Polach, H.V.K. Diyabalanage, C.J. Lovely, J. Am. Chem. Soc. 125 (2003) 9270.
[25] K. Rangan, M. Fianchini, S. Singh, H.V.R. Dias, Inorg. Chim. Acta 362 (2009) 4347.
[26] M.M. Diaz-Requejo, P.J. Perez, Chem. Rev. 108 (2008) 3379.
[27] N.V. Kulkarni, A. Das, N.B. Jayaratna, M. Yousufuddin, H.V.R. Dias, Inorg. Chem. 54 (2015) 5151.
[28] C.J. Lovely, J.A. Flores, X. Meng, H.V.R. Dias, Synlett (2009) 129.
[29] N.V. Kulkarni, C. Dash, N.B. Jayaratna, S.G. Ridlen, S. Karbalaei Khani, A. Das, X. Kou, M. Yousufuddin, T.R. Cundari, H.V.R. Dias, Inorg. Chem. 54 (2015) 11043.
[30] S.M. Gorun, Z. Hu, R.T. Stibrany, G. Carpenter, Inorg. Chim. Acta 297 (2000) 383.
[31] Z. Hu, R.D. Williams, D. Tran, T.G. Spiro, S.M. Gorun, J. Am. Chem. Soc. 122 (2000) 3556.
[32] Z. Hu, G.N. George, S.M. Gorun, Inorg. Chem. 40 (2001) 4812.
[33] J. Nakazawa, S. Terada, M. Yamada, S. Hikichi, J. Am. Chem. Soc. 135 (2013) 6010.
[34] M. Pellei, G. Papini, G.G. Lobbia, S. Ricci, M. Yousufuddin, H.V.R. Dias, C. Santini, Dalton Trans. 39 (2010) 8937.
[35] T.F. van Dijkman, M.A. Siegler, E. Bouwman, Dalton Trans. 44 (2015) 21109.
[36] N. Zhao, J.C. Bullinger, M.J. Van Stipdonk, C.L. Stern, D.M. Eichhorn, Inorg. Chem. 47 (2008) 5945.
[37] J. Urbano, T.R. Belderrain, M.C. Nicasio, S. Trofimenko, M.M. Diaz-Requejo, P.J. Perez, Organometallics 24 (2005) 1528.
[38] U.E. Bucher, A. Currao, R. Nesper, H. Rueegger, L.M. Venanzi, E. Younger, Inorg. Chem. 34 (1995) 66.
[39] E. Del Ministro, O. Renn, H. Rueegger, L.M. Venanzi, U. Burckhardt, V. Gramlich, Inorg. Chim. Acta 240 (1995) 631.
[40] U. Fekl, R. van Eldik, S. Lovell, K.I. Goldberg, Organometallics 19 (2000) 3535.
[41] M.A. Fuentes, A. Olmos, B.K. Munoz, K. Jacob, M.E. Gonzalez-Nunez, R. Mello, G. Asensio, A. Caballero, M. Etienne, P.J. Perez, Chem. Eur. J. 20 (2014) 11013.
[42] K. Fujisawa, M. Yoshida, Y. Miyashita, K.-I. Okamoto, Polyhedron 28 (2009) 1447.
[43] C.K. Ghosh, J.K. Hoyano, R. Krentz, W.A.G. Graham, J. Am. Chem. Soc. 111 (1989) 5480.
[44] R. Han, P. Ghosh, P.J. Desrosiers, S. Trofimenko, G. Parkin, J. Chem. Soc., Dalton Trans. (1997) 3713.
[45] H.K. Joshi, M.E. Arvin, J.C. Durivage, N.E. Gruhn, M.D. Carducci, B.L. Westcott, D. L. Lichtenberger, J.H. Enemark, Polyhedron 23 (2004) 429.
[46] O. Renn, L.M. Vananzi, A. Marteletti, V. Gramlich, Helv. Chim. Acta 78 (1995) 993.
[47] N. Romero, L. Vendier, C. Dinoi, M. Etienne, Dalton Trans. 43 (2014) 10114.
[48] E.R. Sirianni, G.P.A. Yap, K.H. Theopold, Inorg. Chem. 53 (2014) 9424.
[49] T.F. van Dijkman, M.A. Siegler, E. Bouwman, Eur. J. Inorg. Chem. (2016) 2586.
[50] H.V.R. Dias, T.K.H.H. Goh, Polyhedron 23 (2004) 273.
[51] E.L. Elliott, G.A. Hernandez, A. Linden, J.S. Siegel, Org. Biomol. Chem. 3 (2005) 407.
[52] H.V.R. Dias, Z. Wang, W. Jin, Inorg. Chem. 36 (1997) 6205.
[53] A. Loas, S.M. Gorun, Eur. J. Inorg. Chem. (2016) 2648.
[54] G.R. Fulmer, A.J.M. Miller, N.H. Sherden, H.E. Gottlieb, A. Nudelman, B.M. Stoltz, J.E. Bercaw, K.I. Goldberg, Organometallics 29 (2010) 2176.
[55] A.J. Lupinetti, S.H. Strauss, G. Frenking, Progress Inorg. Chem. 49 (2001) 1.
[56] S.L. Shufler, H.W. Sternberg, R.A. Friedel, J. Am. Chem. Soc. 78 (1956) 2687.
[57] Y. Souma, J. Iyoda, H. Sano, Inorg. Chem. 15 (1976) 968.
[58] R. Gava, A. Olmos, B. Noverges, T. Varea, E. Álvarez, T.R. Belderrain, A. Caballero, G. Asensio, P.J. Pérez, ACS Catal. 5 (2015) 3726.
[59] H.V.R. Dias, M. Fianchini, Angew. Chem. Int. Ed. 46 (2007) 2188.
[60] A. Bayler, A. Schier, G.A. Bowmaker, H. Schmidbaur, J. Am. Chem. Soc. 118 (1996) 7006.
[61] M.A. Omary, M.A. Rawashdeh-Omary, M.W.A. Gonser, O. Elbjeirami, T. Grimes, T.R. Cundari, H.V.K. Diyabalanage, C.S.P. Gamage, H.V.R. Dias, Inorg. Chem. 44 (2005) 8200.
[62] K. Fujisawa, S. Imai, Y. Moro-oka, Chem. Lett. (1998) 167.
[63] C. Santini, G. Gioia Lobbia, C. Pettinari, M. Pellei, G. Valle, S. Calogero, Inorg. Chem. 37 (1998) 890.
[64] G.R. Miller, A.W. Yankowsky, S.O. Grim, J. Chem. Phys. 51 (1969) 3185.
[65] M. Kruck, M.P. Munoz, H.L. Bishop, C.G. Frost, C.J. Chapman, G. Kociok-Köhn, C. P. Butts, G.C. Lloyd-Jones, Chem. Eur. J. 14 (2008) 7808.
[66] J.-C. Hierso, Chem. Rev. 114 (2014) 4838.
[67] S. Alvarez, Dalton Trans. 42 (2013) 8617.
[68] G. Gioia Lobbia, J.V. Hanna, M. Pellei, C. Pettinari, C. Santini, B.W. Skelton, A.H. White, Dalton Trans. (2004) 951.
[69] C. Santini, G. Gioia Lobbia, M. Pellei, C. Pettinari, G. Valle, S. Calogero, Inorg. Chim. Acta 282 (1998) 1.
[70] K.-T. Youm, S. Huh, Y.J. Park, S. Park, M.-G. Choi, M.-J. Jun, Chem. Commun. (2004) 2384.
[71] O. Kühl, Phosphorus-31 NMR Spectroscopy, Springer, Berlin, 2008.
[72] M. Sheldrick George, Acta Cryst. A 64 (2008) 112.
[73] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, J. Appl. Crystallogr. 42 (2009) 339.