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Synthesis and characterization of molybdenum and tungsten complexes containing tris(diphenylphosphino)methane (tdppm)

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ABSTRACT

Reaction of tris(diphenylphosphino)methane, $(Ph_2P)_3CH$ (tdppm) with 1 equivalent of $M(CO)_3(EtCN)_3$ (M = Mo **1a**, M = W **1b**) affords $[Mo\{\eta^2\text{-}(Ph_2P)_3CH\}(CO)_3(EtCN)]$ **2a** and $[W\{\eta^2\text{-}(Ph_2P)_3CH\}(CO)_3(EtCN)]$ **2b**, respectively. Single crystal structure determinations were performed for complexes **2a** and **2b**. Both structures adopt a distorted octahedral geometry about Mo and W atoms, with one CO and EtCN group occupying an axial position, while the phosphine ligand and two CO ligands occupy the equatorial positions. To our knowledge this is the first structurally-characterized W complex containing the tdppm ligand.

One of the primary goals of synthetic organometallic or coordination chemists is to control the interactions between metals and ligands. Towards this end, over the years chemists have prepared ligands with a wide range of features designed to achieve their particular purposes. As a common example, ligands have been carefully crafted with precise steric features designed to control reactivity at a metal site. As another generalized example, ligands have been synthesized that are multidentate in order to again control reactivity at the metal site, or perhaps to force two metals to interact. The varieties of ligands and ligand–metal interactions that are possible appear to be virtually unlimited. In this submission we report on some new synthetic Mo and W chemistry of a known multidentate ligand, tris(diphenylphosphino)methane, $(Ph_2P)_3CH$, or tdppm [1,2]. It has been well-documented in the organometallic literature, as well as in the Cambridge Structural Database (CSD) [3], that this tridentate tdppm ligand can act in various manners towards transition metals, coordinating as either a bridging [4,5], bridging–chelating [6–10], chelating [11–15], or simply as a monodentate ligand [12]. In particular, there has been historical interest in using the three P atoms of tdppm as a "capping" ligand for metals. We also note that the structure of the tdppm ligand itself has also been reported [16].

In an electronic sense, there are numerous examples of chelating di-phosphorus ligands that are capable of donating lone pairs of electrons to a single metal atom in a σ- rather than π-fashion. As well, the σ-donor ligative behavior of various tri, tetra-, or higher chelating phosphorus ligands has also been developed for coordination to both mono- and multi-metallic complexes (illustrative examples including tdppm are shown in Fig. 1). Herein, we report the synthesis and characterization of Group 6 (Mo and W) metal complexes containing the tdppm ligand that possess the general formula $[M\{\eta^2\text{-}(Ph_2P)_3CH\}(CO)_3(EtCN)]$ where M = Mo **2a**, and W **2b**. Interestingly, complexes of tdppm with various transition metals have been structurally characterized as noted above; however, crystallographically-characterized tdppm complexes containing two of the most common Group 6 metals – Mo and W – are rare (Mo) or non-existent (W). In the rare cases of Mo, tdppm has only been used to bridge a Mo–Mo quadruple bond [17], and to serve as a bridging ligand to Mo and Au in a series of heterometallic compounds [18]. A search of the CSD (version 5.32, November 2011 update) indicates that there are no directly bound tdppm-W complexes that have been structurally characterized. Surprisingly, the starting tdppm-Mo complexes prior to Au complexation have also not been structurally-characterized. In this paper we help fill the void in the solid-state characterization of these complexes and also utilize a Group 6 starting reagent – $M(CO)_3(EtCN)_3$ – that leaves a weakly-coordinated EtCN moiety on the complex that is available for further substitution chemistry.

As outlined in Scheme 1, reaction of $M(CO)_3(EtCN)_3$ (M = Mo **1a**, W **1b**) with tdppm ligand in a 1:1 molar ratio in proprionitrile/dichloromethane or toluene resulted in the formation of complexes $[Mo\{\eta^2\text{-}(Ph_2P)_3CH\}(CO)_3(EtCN)]$ **2a** and $[W\{\eta^2\text{-}(Ph_2P)_3CH\}(CO)_3(EtCN)]$ **2b** in 65% and 70% yields, respectively [19]. In order to speed up each reaction, brief sonication of the reaction mixtures occurred during which time precipitates were formed. After sonication, each reaction mixture was stirred at room temperature for an additional 12 h. The precipitates were removed by filtration and washed with

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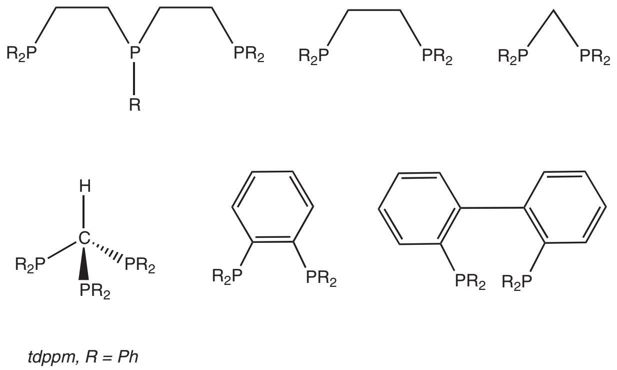

Fig. 1. Examples of multidentate phosphines (R = alkyl, aryl), including tdppm.

Scheme 1. Preparation of tdppm complexes of Mo and W.

diethyl ether and dried. Analytically-pure crystals of **2a** and **2b** were grown at room temperature from a concentrated solution of each complex in dichloromethane.

Complex **2a** was fully characterized by a combination of ^{1}H, ^{13}C, and ^{31}P NMR spectroscopies, elemental analysis, IR, and single crystal X-ray diffraction. Elemental analysis of complex **2a** is consistent with the calculated values for the proposed structure. The ^{1}H NMR analysis of **2a** revealed a triplet at 1.02 ppm and a quartet at 1.32 ppm with $^{3}J_{H-H} = 7.5$ Hz, consistent with the $-CH_2CH_3$ group. As well, a singlet observed at 4.75 ppm can be assigned to the hydrogen that is attached to the tertiary carbon of tdppm ligand. The ^{13}C NMR spectrum of **2a** in CD_2Cl_2 revealed peaks that are consistent with $-C_6H_6$, $-CH_2CH_3$, and $-CN$ groups; however, the chemical shift corresponding to the $-CO$ group was not observed. The inability to see this peak is not surprising and may be due to low signal-to-noise in the absence of ^{13}C-labeled carbonyls. At ambient temperature, the ^{31}P NMR spectrum of **2a** in CD_2Cl_2 exhibits a doublet at 24.2 ppm and a triplet at -23.0 ppm with $^{2}J_{P-P} = 23$ Hz, indicating two different phosphorus environments. This suggests that phosphorus atoms of the ligand are bound to the metal in a bidentate fashion with one free phosphine arm. The υ_{CO} frequencies for **2a** are observed at 1890 cm^{-1} and 1770 cm^{-1}, very similar to those observed by Chatt and co-workers [20] and Fernandez and co-workers [18] for related complexes utilizing Group 6 hexacarbonyls as the starting reagents.

As with **2a**, **2b** was also fully characterized by a combination of ^{1}H, and ^{31}P NMR spectroscopy, elemental analysis, IR and X-ray crystallography. ^{13}C NMR data were not obtained because of the poorer solubility of complex **2b**. In the ^{1}H NMR spectrum the characteristic singlet observed at 5.60 ppm is found and can be assigned to the hydrogen that is attached to the tertiary carbon of tdppm ligand. Similarly to complex **2a**, ^{31}P NMR analysis of complex **2b** in CD_3OCD_3 exhibits a doublet at 2.1 ppm and a triplet at -23.1 ppm with $^{2}J_{P-P} = 25$ Hz, indicating again that the two phosphorus atoms are bound to the metal in a bidentate fashion. Elemental analysis for **2b** was consistent with the calculated values for %N and %H; however, a slight difference in %C between experimental and calculated was observed. IR analysis for complex **2b** indicated strong υ_{CO} absorbances at 1930 cm^{-1} and 1785 cm^{-1}, again similar to those reported by Chatt and co-workers [20].

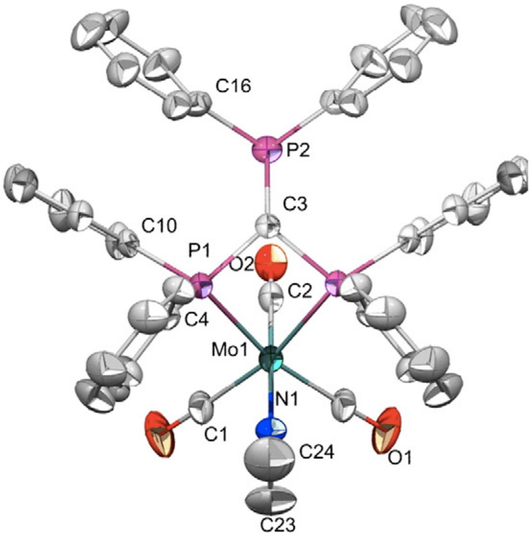

Fig. 2. Molecular structure of **2a** with thermal ellipsoids projected at 50% level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Mo1−C1 1.977(2), Mo1−C2 1.946(3), Mo1−N1 2.201(3), Mo1−P1 2.4962(6); P1−Mo1−P2 67.24(3), C1−Mo1−C2 87.46(10), N1−Mo1−C2 178.57(11), C1−Mo1−P1 99.47(7), N1−Mo1−P1 88.51(6), C10−P1−C4 100.16(10), C10−P1−Mo1122.76(7).

Single crystal X-ray analyses [21,22] of **2a** and **2b** definitively indicated that the tdppm ligand had coordinated to the metal in a bidentate fashion for both complexes, leaving one phosphine arm free [23]. These structures represent rare examples of structurally characterized, tdppm complexes of Group 6 metals that do not contain any additional metals. As well, each contains a residual EtCN ligand that is more labile than the CO ligand. Complex **2a** crystallizes in the orthorhombic crystal system, space group *Pnma*, and contains a mirror plane of symmetry bisecting through P(2), C(3), C(22)-C(24) and Mo(1). As depicted in Fig. 2 complex **2a** adopts a distorted octahedral geometry in the solid-state. This distortion is mostly attributed to the restricted bite angle of the chelating phosphine [P1-Mo1-P1 is 67.24(3)°]. The bite angle for complex **2a** is comparable to those found for the molybdenum complexes containing chelated phosphine ligands [18,23,24]. However, this bite angle is smaller than that reported by Beckett and co-workers [25] for the square-planar complex $[Pt\{PPh_2)_2CHPPh_2\}_2][BF_4]_2$. Briefly, the structure consists three CO ligands with Mo−C1 and Mo−C2 bond distances of 1.977(2) Å and 1.946(3) Å, respectively. The Mo−C bond distances for **2a** are within the range of values for molybdenum carbonyl complexes reported in the literature [26–28]. The bond lengths Mo1−P1 and Mo1−N1 are 2.4962(6) Å and 2.201(3) Å, respectively. Both of these values comparable favorably to other reported values for Mo complexes in the literature [12–15]. One of the CO ligands and the EtCN group is *trans* to each other and occupies axial positions, while the chelating phosphine ligand and two CO ligands occupy the four remaining equatorial positions. The EtCN ligand is located in the coordination position to allow for the mirror plane symmetry found the molecule.

Similarly to **2a**, the W atom in **2b** is coordinated by three carbonyl groups, EtCN, and the two phosphorus groups from the tdppm ligand; hence, it adopts a distorted octahedral geometry in the solid state (Fig. 3). Analysis shows that **2b** is isostructural to **2a** and crystallizes in the orthorhombic crystal system, space group *Pnma.* Similar to **2a**, complex **2b** also contains a mirror plane of symmetry bisecting through P2, C2, O2, EtCN, and W1. The restricted bite angle of the phosphine, P1-W1-P1 of 67.23(5)° is comparable with those reported in the literature for tungsten compounds containing the related ligand bis(diphenylphosphino)methane, $(Ph_2P)_2CH_2$ [20]. The chelate ring formed by W, P(1), C(3), and P(1) in complex **2b** is nearly planar.

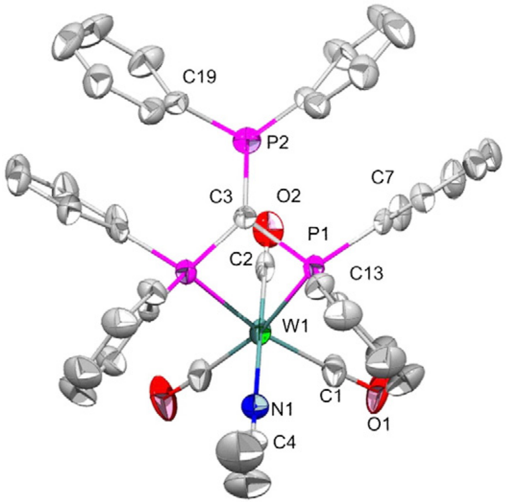

Fig. 3. Molecular structure of **2b** with thermal ellipsoids projected at 50% level. Hydrogen atoms have been omitted for clarity. Selected bond distances (A) and angles (°): W1 – C1 1.971(5), W1 – C2 1.952(7), W1 – N1 2.179(6) , W1 – P1 2.4866(10); C2 – W1 – C1 88.17(18), C2 – W1 – N1 178.8(2), C1 – W1 – N1 91.04(17), C1 – W1 – P1 99.07(13), P1 – W1 – P1 67.23(5), C13 – P1 – W1 118.94(14), C7 – P1 – W1 122.51(13).

The structure consists of W1 – C1 and W1 – C2 distances of 1.971(5) Å and 1.952(7) Å, respectively. The W – C bond lengths of complex **2b** are closely related to those previously observed in the literature [29]. Aditionally, the W1 – P1 and W1 – N1 bond lengths are 2.4866(10) Å and 2.179(6) Å, respectively. The W – P bond distance found in complex **2b** is slightly shorter than the values observed in other tungsten complexes [24,29,30].

In summary, we have prepared and fully-characterized rare Mo and W metal complexes that contain tdppm ligand acting as a traditional bidentate ligand. The coordination mode observed in complexes **2a** and **2b** by X-ray crystallography confirms that the tdppm ligand acts as a chelating ligand to Group 6 metals, with three CO's and one EtCN ligand filling out the distorted octahedral coordination sphere. The present work has helped fill the void in solid-state characterization of directly bound tdppm-W and Mo complexes. Importantly, using a Group 6 starting material $M(CO)_3(EtCN)_3$ that eventually results in a weakly coordinated EtCN group remaining on the complex, clearly has an advantage over $M(CO)_6$-derived complexes in that further substitution chemistry is facilitated.

Acknowlegments

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Appendix A. Supplementary data

The structural data for **2a** and **2b** have been deposited as CCDC 851857 and 851858. These data are available free of charge and can be obtained from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data to this article can be found online at doi:10.1016/j.inoche.2012.01.030.

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[19] Preparation of **2a**: the tpddm $(Ph_2P)_3CH$ ligand (0.30 g, 0.52 mmol) was added to a 100 ml Schlenk flask containing 10 ml of toluene in an inert atmosphere. This was followed by dropwise addition of **1a** (0.18 g, 0.52 mmol) dissolved in 10 ml of propionitrile. The solution was sonicated for 5 min and then allowed to stir for additional 12 h. The precipitate formed was separated from the solution using a fine filter frit. The solid was washed with diethyl ether (10 ml × 3) then dried under vacuum. The yield of **2a** was 0.30 g [65% isolated, crystalline product based on $Mo(CO)_3(EtCN)_3$]. Analytically pure crystals of **2a** were obtained by recrystallization from CH_2Cl_2. Complex **2a** decomposed at 188 °C. ^1H NMR (CD_2Cl_2, 300 MHz, ppm): 6.43–7.76 (m, Ar-H, 30H), 4.75 (s, CH, 1H), 1.32 (q, $^3J_{H-H}=7.5$ Hz, CH_2, 2H), 1.03 (t, $^3J_{H-H}=7.5$ Hz, CH_3, 3H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75 MHz, ppm): 175.2, 154.3, 129.5, 124.9, 59.3, 58.6, 58.1. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.49 MHz, ppm): 24.2 (d, $^2J_{P-P}=23$ Hz), −23.0 (t, $^2J_{P-P}=23$ Hz). Anal. Calcd: C 64.27, H 4.52, N 1.74. Found: C 64.25, H 4.37, N 1.39. IR: $\upsilon_{CO}=1930$, 1785 cm^{-1}. Compound **2b** was prepared similarly in 70% yield. **2b** decomposed at 180 °C. ^1H NMR (CD_3COCD_3, 300 MHz, ppm): 6.8–7.9 (m, Ar-H, 30H), 5.60 (s, CH, 1H), 2.57 (q, $^3J_{H-H}=6.6$ Hz, CH_2, 2H), 1.13 (t, $^3J_{H-H}=6.6$ Hz, CH_3, 3H). $^{31}P\{^1H\}$ NMR (CD_3COCD_3, 121.49 MHz, ppm): 2.1 (d, $^2J_{P-P}=25$ Hz), −23.1 (t, $^2J_{P-P}=25$ Hz). Anal. Calcd: C 57.80, H 4.07, N 1.57. Found: C 56.84, H 4.19, N 1.25. IR: $\upsilon_{CO}=1890$, 1770 cm^{-1}.
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[22] Diffraction data were obtained on a Bruker X8 ApexII κ-axis diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda=0.71073$ Å) and a CCD camera. The intensity data were corrected for Lorentz and polarization effects. The structure was solved using direct methods and refined by full-matrix least-squares methods on F^2. All hydrogens were added in idealized positions and not allowed to vary. Crystal structure analysis for **2a**: $C_{43}H_{36}MoNO_3P_3$, F_w 803.63, orthorhombic, *Pnma*, $a=16.5384(3)$ Å, $b=20.6593(4)$ Å, $c=11.3661(2)$Å, $\alpha=\beta=\gamma=90°$, $V=3883.48(12)$ Å^3, $Z=4$, $F(000)=1648.0$, $T=188(2)$ K, green rods, 0.25 × 0.07 × 0.07 mm^3, $\mu=0.501$ mm^{-1}, $Dx=1.374$ g/cm^3, 2θ-range 0.998 to 30.56°, independent reflections 84431, wR (all data) 0.0885, $R_1[I>2(I)]$ 0.0753. Crystal structure analysis for **2b**: $C_{43}H_{35}WNO_3P_3$, F_w 891.49, orthorhombic, *Pnma*, $a=16.4570(5)$, $b=20.7161(6)$, $c=11.3192(4)$ Å, $\alpha=\beta=\gamma=90°$, $V=3859.0(2)$ Å^3, $Z=4$, $F(000)=1776.0$, $T=188(2)$ K, yellow planks, 0.25 × 0.02 × 0.02 mm^3, $\mu=3.158$ mm^{-1}, $Dx=1.534$ g/cm^3, 2θ-range 0.998 to 28.360°, independent reflections 4929, wR (all data) 0.0734, $R_1[I>2(I)]$ 0.0618.
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