

Unusual difference in the reactivity of seven-coordinated Mo(II) and W(II) carbonyl complexes, $[M_2(CO)_3(NCCH_3)_2]$ with derivatised-dppm, $Me_3SiN=PPh_2CH_2PPh_2^\dagger$

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The reaction of $[Mo(CO)_3I_2(NCCH_3)_2]$ with a stoichiometric amount of $Me_3SiN=PPh_2CH_2PPh_2$ gives an octahedral complex, $[Mo_2(CO)_3(\eta^2-N=PPh_2CH_2PPh_2)]$ by the metathetical elimination of Me_3SiI . Interestingly, similar reaction of the analogous tungsten complex gives a seven-coordinated complex, $[W_2(CO)_3(\eta^2-Me_3SiN=PPh_2CH_2PPh_2)]$ which ultimately hydrolyses to give an amide complex, $[W(CO)_3I_2(\eta^2-HN=PPh_2CH_2PPh_2)]$. The complexes have been characterised by microanalysis, IR and NMR (1H and ^{31}P) spectroscopic data.

Keywords: $Mo(CO)_3I_2(NCCH_3)_2$, $Me_3SiN=PPh_2CH_2PPh_2$

The transition metal chemistry of heterodifunctional ligands of the type $Ph_2PQPh_2P=NR$ ($Q=CH_2$, $R=SiMe_3$, C_6F_4CN ; $^{1-3}$ $Q=N(alkyl)$, $R=SiMe_3$, $P(O)(OPh)_2$, C_6F_4CN , C_6F_4CHO etc.; 4,5 $Q=C_6H_4$, $R=SiMe_3$) is well documented. We have previously described synthetic, spectroscopic and structural investigations of the transition metal complexes of a variety of bis(phosphine) ligands and their functionalised derivatives. All these ligands showed remarkable versatility in their coordination behavior. As a part of our study on phosphorus donor ligands and their organometallic chemistry, $^{7-10}$ we have investigated the reaction of $Me_3SiN=PPh_2CH_2PPh_2$ with seven coordinated Mo(II) and W(II) derivatives $[M_2(CO)_3(NCCH_3)_2]$ ($M=Mo$ or W) and isolated two totally different complexes, viz. octahedral $[MoI_2(CO)_3(\eta^2-N=PPh_2CH_2PPh_2)]$ (**1**) and seven-coordinated $[W_2(CO)_3(\eta^2-Me_3SiN=PPh_2CH_2PPh_2)]$ (**2**) which have been characterised by microanalyses and IR and NMR (1H and ^{31}P) spectroscopy.

The reaction of an equimolar quantity of $Me_3SiN=PPh_2CH_2PPh_2$ with $[MoI_2(CO)_3(NCCH_3)_2]$ (generated *in situ*) 11 in CH_2Cl_2 solution at $25^\circ C$ gives an octahedral complex, $[MoI_2(CO)_3(\eta^2-N=PPh_2CH_2PPh_2)]$ (**1**) with the elimination of Me_3SiI . In contrast the reaction of $Me_3SiN=PPh_2CH_2PPh_2$ with $[W_2(CO)_3(NCCH_3)_2]$ (generated *in situ*) gives the new seven-coordinated complex, $[W_2(CO)_3(\eta^2-HN=PPh_2CH_2PPh_2)]$ (**2**) in good yield. The complexes **1** and **2** are highly air and moisture sensitive even in the solid state and decompose to give insoluble dark brown complexes that may contain metals in their higher oxidation states. The molybdenum complex readily loses one of the coordinated iodide ligands as Me_3SiI to form an octahedral complex whereas the tungsten complex retains the seven-coordination at the metal centre. However, the complex readily loses its

Me_3Si - group to give an NH bond, but surprisingly keeps both the iodide ligands intact as indicated by spectroscopic and analytical data. The IR spectrum shows a band at 3345 cm^{-1} clearly indicating the elimination of the Me_3Si - group with the formation of an NH bond. Further elucidation of the structures of complexes **1** and **2** is based on elemental analyses, IR and 1H and ^{31}P NMR spectroscopic data.

The infrared spectra of complexes **1** and **2** show three carbonyl vibrations in the region $2023\text{--}1889\text{ cm}^{-1}$, as expected [12]. The ^{31}P NMR spectrum of **1** shows two well resolved doublets at 51.4 and 56.2 ppm respectively for P(III) and P(V) centres with a $^2J_{PP}$ coupling of 35 Hz. The tungsten complex in its ^{31}P NMR spectrum also shows two sharp doublets at 35.7 and 54.8 ppm respectively for P(III) and P(V) centres with a $^2J_{PP}$ coupling of 33 Hz. The phosphorus(III) centre shows a $^1J_{PW}$ coupling of 213.7 Hz, whereas the phosphorus(V) centre shows a $^3J_{PW}$ value of 12.4 Hz [13]. The 1H NMR spectra of complexes **1** and **2** are thus consistent with the proposed structures.

Experimental

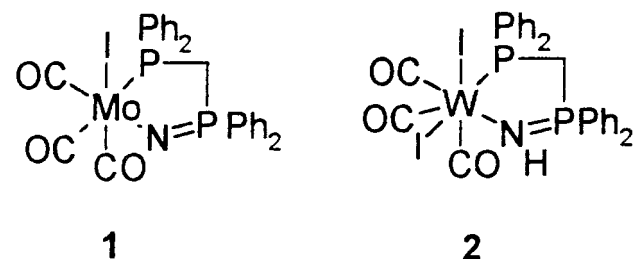
Reaction of $Me_3SiN=PPh_2CH_2PPh_2$ with $[M_2(CO)_3(NCCH_3)_2]$: To a stirred solution of $M_2(CO)_3(NCCH_3)_2$ (prepared *in situ* at $0^\circ C$; 10 mmol) in 25 ml of CH_2Cl_2 was added a solution of $Me_3SiN=PPh_2CH_2PPh_2$ (10 mmol) in 20 ml CH_2Cl_2 dropwise with vigorous stirring. Stirring was continued for 30 min, and the solution was filtered through Celite. Concentration of the resulting solution under reduced pressure followed by the addition of *n*-hexane gave crystalline products **1** and **2** in good yield.

$[MoI_2(CO)_3(\eta^2-N=PPh_2CH_2PPh_2)]$ (**1**): Dark red crystals. m.p. $126^\circ C(d)$. yield 78%. Anal. Calc. for $C_{28}H_{22}INO_3P_2Mo$: C, 47.68; H, 3.14; N, 1.98. Found: C, 47.59; H, 3.02; N, 1.89%. IR(mull): 2021, 1987, 1900 cm^{-1} (ν_{CO}). 1H NMR ($CDCl_3$): δ 7.32, 7.52, 7.68 (m, 20H); 3.64 (t, 2H, $^2J_{PH}=10$ Hz). ^{31}P NMR ($CDCl_3$): δ P(III) 51.8 (d); P(V) 56.3 (d); $^2J_{PP}=35$ Hz.

$[W_2(CO)_3(\eta^2-HN=PPh_2CH_2PPh_2)]$ (**2**): Orange red crystals. m.p. $142^\circ C(d)$. yield 78%. Anal. Calc. for $C_{28}H_{23}I_2NO_3P_2W$: C, 36.51; H, 2.51; N, 1.52. Found: C, 36.23; H, 2.47; N, 1.42%. IR(mull): 2017, 1954, 1885 cm^{-1} (ν_{CO}); 3344 cm^{-1} (ν_{NH}). 1H NMR ($CDCl_3$): δ : δ 7.30, 7.55, 7.72 (m, 20H); 3.71 (t, 2H, $^2J_{PH}=11.4$ Hz). ^{31}P NMR ($CDCl_3$): δ P(III) 35.8 (d); P(V) 54.6 (d); $^2J_{PP}=33$ Hz; $^1J_{PW}=215$ Hz; $^2J_{PW}=12.2$ Hz.

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