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1,1′-Bis(diphenylphosphino)ferrocene Complexes of Molybdenum(II) and Tungsten(II)

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The unusual bidentate phosphine ligand 1,1′-bis(diphenylphosphino)ferrocene has often been used as a ligand in organometallic chemistry. Cullen and co-workers have very recently reported the synthesis of a range of ferrocenylphosphine complexes, [PdCl_2(L–L)], [Rh(L–L)(η^4-norbornadiene)], and [NiCl_2(L–L)] {L–L = Fe(η^5-$C_5H_4PR^1R^2$)(η^5-$C_5H_4PR^3R^4$) (R^1–R^4 = Ph or CMe_3)} [1]. In view of the wide range or organometallic complexes of the type [$MX_2(CO)_3L_2$] (M = Mo and W; X = Cl, Br and I; L = phosphines) which are known [2], it is surprising that complexes of this type containing the bidentate phosphine ligand 1,1′-bis(diphenylphosphino)ferrocene have not been reported. In this communication we wish to report the synthesis of the new diiodide complexes [$MI_2(CO)_x(Ph_2PFePPh_2)$] {M = Mo, x = 2 or 3; M = W, x = 3; $Ph_2PFePPh_2$ = 1,1′-bis(diphenylphosphino)ferrocene}, and the new compound [$MoCl_2(CO)_2(Ph_2PFePPh_2)_2$].

Experimental

[$MI_2(CO)_3(NCMe)_2$] [3] and [Mo(μ-Cl)Cl$(CO)_4$]$_2$ [4] were prepared according to literature methods, and 1,1′-bis(diphenylphosphino)ferrocene was purchased from Strem Chemicals, Inc.

^{1}H NMR spectra were recorded on a Jeol FX60 NMR spectrometer (all spectra were calibrated against tetramethylsilane). Infrared spectra were recorded on a Perkin-Elmer 197 infrared spectrophotometer. Elemental analyses for carbon, hydrogen and nitrogen were recorded on a Carlo Erba Elemental Analyser MOD1106 (using a helium carrier gas).

[$MoI_2(CO)_2(Ph_2PFePPh_2)$]·$CH_2Cl_2$ (1)

To $MoI_2(CO)_3(NCMe)_2$ (0.298 g, 0.578 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry argon was added $Ph_2PFePPh_2$ (0.32 g, 0.577 mmol). The mixture was left stirring for 5 min after which time an orange precipitate was observed in the solution. This was filtered and dried under vacuum to afford [$MoI_2(CO)_2(Ph_2PFePPh_2)$]·$CH_2Cl_2$ (yield = 0.50 g, 83%). *Anal.* Calc. for $C_{37}H_{30}FeI_2MoO_2P_2Cl_2$: C, 42.5; H, 2.9. Found. C, 42.7; H, 3.1%. At room temperature the ^{1}H NMR spectrum ($CDCl_3$) showed resonances at δ = 7.57 (brm, 20H, Ph), 5.3 (s, 2H, CH_2Cl_2), 4.47 (brm, 8H, C_5H_4P). IR spectrum ($CHCl_3$): ν(CO) cm^{-1} = 1920(s) and 1858(s). The complex [$MoI_2(CO)_2(Ph_2PFePPh_2)$]·NCMe was prepared in a similar manner from reaction of [$MoI_2(CO)_3(NCMe)_2$] and $Ph_2PFePPh_2$ in acetonitrile.

[$MoI_2(CO)_3(Ph_2PFePPh_2)$]·0.5$CH_2Cl_2$ (2)

In a precipitate of [$MoI_2(CO)_2(Ph_2PFePPh_2)$]·NCMe (0.21 g, 0.21 mmol) in CH_2Cl_2 carbon monoxide was bubbled for 60 min. The precipitate dissolved and gave a red solution which upon removal of solvent gave red crystals of [$MoI_2(CO)_3(Ph_2PFePPh_2)$]·0.5$CH_2Cl_2$ (yield = 0.14 g, 68%). *Anal.* Calc. for $C_{37.5}H_{29}FeI_2MoO_3P_2Cl$: C, 43.7; H, 2.8. Found: C, 43.7; H, 3.1%. At room temperature the ^{1}H NMR spectrum showed resonances at δ = 7.47 (brm, 20H, Ph), 5.3 (s, 1H, CH_2Cl_2), 4.47 (brm, 8H, C_5H_4P) IR spectrum ($CHCl_3$). ν(CO) cm^{-1} = 2015(s), 1965(s) and 1896(m).

[$WI_2(CO)_3(Ph_2PFePPh_2)$] (3)

To $WI_2(CO)_3(NCMe)_2$ (0.32 g, 0.53 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry argon was added $Ph_2PFePPh_2$ (0.294 g, 0.53 mmol), and the mixture was stirred for 15 min. Removal of the solvent *in vacuo* afforded the analytically pure complex $WI_2(CO)_3(Ph_2PFePPh_2)$ (yield 0.49 g, 86%). *Anal.* Calc. for $C_{37}H_{28}FeI_2O_3P_2W$: C, 41.3; H, 2.6. Found: C, 41.4; H, 2.8%. At room temperature the ^{1}H NMR spectrum ($CDCl_3$) showed resonances at δ = 7.44 (m, 20H, Ph), 4.67 (brs, 4H, P–CH), 4.34 (brs, 4H, C–CH). IR spectrum ($CHCl_3$): ν(CO) cm^{-1} = 2025(s), 1948(s) and 1906(s).

[$MoCl_2(CO)_2(Ph_2PFePPh_2)_2$] (4)

[Mo(μ-Cl)Cl$(CO)_4$]$_2$ was prepared from $Mo(CO)_6$ (0.5 g, 1.9 mmol) by reaction with Cl_2 at −78 °C. To [Mo(μ-Cl)Cl$(CO)_4$]$_2$ in a propanone (20 cm^3) solution of $Ph_2PFePPh_2$ (1.05 g, 1.9 mmol) was added, and the mixture was stirred for 12 h after which time a deep blue precipitate was observed in the solution. This was filtered and dried under vacuum (yield 0.45 g, 18%). *Anal.* Calc. for $C_{70}H_{56}Cl_2Fe_2MoO_2P_4$. C, 63.1; H, 4.2. Found. C, 63.4, H, 4.1%. IR spectrum ($CHCl_3$)· ν(CO) cm^{-1} = 1962(m) and 1880(s).

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Results and Discussion

Microanalytical data (C, H and N), infrared spectroscopy, and ^{1}H NMR spectroscopy (see 'Experimental') support the formulation of the new complexes **1**–**4**. It is interesting to note the bidentate phosphine ligand $Ph_2P(CH_2)_2PPh_2$ (dppe) reacts at room temperature [5] with $[Mo(\mu\text{-}I)I(CO)_4]_2$ to give the seven-coordinate complex $[MoI_2(CO)_3(dppe)]$, whereas reaction of $Ph_2PFePPh_2$ with $[MoI_2(CO)_3(NCMe)_2]$ in CH_2Cl_2 to give the '16-electron' complex $[MoI_2(CO)_2(Ph_2PFePPh_2)]\cdot CH_2Cl_2$ (the CH_2Cl_2 solvate is confirmed by repeated elemental analyses and ^{1}H NMR spectroscopy). This is probably due to the large 'cone-angle' [6] of $Ph_2PFePPh_2$, and it has been reported [1] that the $[NiX_2(Ph_2PFePPh_2)]$ (X = Cl or Br) complexes have tetrahedral geometry which has been suggested to be due to the steric bulk of the $Ph_2PFePPh_2$ ligand, which is in contrast to the $[NiX_2(L\text{–}L)]$ {X = Cl and Br; L–L = $Ph_2P(CH_2)PPh_2$ and $Ph_2P(CH_2)_2PPh_2$} complexes which exhibit square-planar geometry [7]. Although other '16-electron' complexes of the type $[MX_2(CO)_2L_2]$ (M = Mo and W; X = Cl, Br and I; L = PPh_3 and PEt_3) are known [8–12], they are more common for molybdenum than tungsten, and hence it is not surprising that reaction of $Ph_2PFePPh_2$ with $[WI_2(CO)_3(NCMe)_2]$ in CH_2Cl_2 gives the seven-coordinate tricarbonyl complex $[WI_2(CO)_3(Ph_2PFePPh_2)]$. The molybdenum complex $[MoI_2(CO)_2Ph_2PFePPh_2)]\cdot NCMe$ can be converted to the seven-coordinate tricarbonyl complex $[MoI_2(CO)_3(Ph_2PFePPh_2)]\cdot 0.5CH_2Cl_2$ (the $0.5CH_2Cl_2$ solvate is confirmed by repeated elemental analyses and ^{1}H NMR spectroscopy) simply by bubbling carbon monoxide through a CH_2Cl_2 solution of $[MoI_2(CO)_2(Ph_2PFePPh_2)]\cdot NCMe$.

It has been noted that the stabilities of the tricarbonyls $[MX_2(CO)_3(dppe)]$ towards further attack by dppe decreases in the order I > Br > Cl and W > Mo, and that $[MoCl_2(CO)_3(dppe)]$ could only be isolated with great difficulty [2]. Hence it is not surprising that equimolar quantities of $[Mo(\mu\text{-}Cl)Cl(CO)_4]_2$ and $Ph_2PFePPh_2$ react in propanone to afford only the seven-coordinate bis($Ph_2PFePPh_2$) complex *cis*-$[MoCl_2(CO)_2(Ph_2PFePPh_2)_2]$ with one of the $Ph_2PFePPh_2$ ligands with bidentate coordination, and the other bonded as a monodentate ligand. Reaction of the dibromo complex $[Mo(\mu\text{-}Br)Br(CO)_4]$ with $Ph_2PFePPh_2$ gave a mixture of products. We are currently investigating the chemistry of these complexes, in particular the catalytic activity in view of the recent work of Bencze and co-workers [13, 14] who have reported that the complexes $[MX_2(CO)_3L_2]$ (M = Mo or W; X = Cl or Br; L = PPh_3 or $AsPh_3$) act as catalysts for the ring opening polymerisation of norbornene.

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