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SYNTHESIS AND CHARACTERISATION OF $[AgL(\mu\text{-}PR_2)M(CO)_5]$, L = 1,10-PHENANTHROLINE OR TRICYCLOHEXYLPHOSPHINE; M = Cr, Mo, W

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Summary

The new heterobimetallic phosphido-bridged compounds $[AgL(\mu\text{-}PR_2)M(CO)_5]$, (L = 1,10-phenanthroline or tricyclohexylphosphine; M = Cr, Mo, W) have been prepared from AgO_3SCF_3, $M(CO)_5PR_2H$ and the ligand L in the presence of Et_2NH or MeO^- as base, and characterized by ^{31}P NMR spectroscopy.

There appear to be no previous reports of silver(I) phosphido complexes, although there are numerous examples of Ag—P-bonded species in coordination complexes of silver(I) with neutral phosphorus ligands (e.g. t-phosphines [1]), as well as with anionic (e.g. phosphito [2] or phosphinito [2]) ligands. We describe here a series of phosphido-bridged silver(I)-Group VIB metal complexes of the type $[Ag(\mu\text{-}PR_2)M(CO)_5]$ with M = Cr, Mo and W.

Experimental

NMR spectra were recorded on a multinuclear Bruker WP-80 spectrometer operating in the FT mode. Chemical analyses were performed on a Heraeus EA 415. The phosphine complexes $M(CO)_5PR_2H$, R = Cy, Cy = cyclohexyl, M = Cr; R = Ph, M = Cr, Mo, W were made as previously described [3] and the other reagents were obtained commercially. The experiments described below were all carried out under nitrogen.

Preparation of $[Ag(phen)(\mu\text{-}PPh_2)Mo(CO_5)]$ (phen = 1,10-phenanthroline)

A solution of AgO_3SCF_3 (103 mg, 0.4 mmol) in a mixture of 0.5 cm^3 of Et_2NH and 1 cm^3 of toluene was cooled to 273 K and $Mo(CO)_5PPh_2H$ (169 mg, 0.4 mmol) was added. The resulting solution was filtered into a solution of 79 mg (0.4 mmol) of 1,10-phenanthroline in 1 cm^3 of CH_2Cl_2. The product crystallized out as yellow needles (81%) upon standing. It decomposes above 130°C.

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Found: C, 49.6; H, 2.6; N, 4.1. $C_{29}H_{18}AgMoN_2O_5P$ calcd.: C, 49.1; H, 2.6; N, 3.9. The following were prepared analogously;

[Ag(phen)(μ-PPh$_2$)Cr(CO)$_5$], dec. 120°C. Found: C, 52.1; H, 2.9; N, 4.2. $C_{29}H_{18}AgCrN_2O_5P$ calcd.: C, 52.4, H, 2.7, N, 4.2%.

[Ag(phen)(μ-PPh$_2$)W(CO)$_5$], dec. 135°C. Found: C, 43.9; H, 2.0; N, 3.5. $C_{29}H_{18}N_2O_5PW$ calcd.: C, 43.7; H, 2.3; N, 3.5%.

Preparation of [Ag(phen)(μ-PCy$_2$)Cr(CO)$_5$]

A solution containing equivalent amounts of AgO_3SCF_3 and $Cr(CO)_5PCy_2H$ in diethylamine/toluene = 1/2 was set aside overnight. After addition of one equivalent of NaOMe the rest of the procedure was as described and gave pale yellow crystals of the product in 40% yield. It decomposes above 135°C. Found: C, 51.1; H, 4.5; N, 4.6. $C_{29}H_{30}AgCrN_2O_5P$ calcd.: C, 51.4; H, 4.5; N, 4.1%.

Preparation of [Ag(PCy$_3$)(μ-PPh$_2$)Mo(CO)$_5$]

A solution of AgO_3SCF_3 (103 mg, 0.4 mmol) in a mixture of 0.5 cm^3 of Et_2NH and 1 cm^3 of toluene was cooled to 273 K and $Mo(CO)_5PPh_2H$ (169 mg, 0.4 mmol) was added. The resulting solution was filtered onto 112 mg (0.4 mmol) of solid PCy_3. The volume of the resulting solution was reduced in vacuo to ca. 0.5 cm^3 and 1 cm^3 of methanol added. The product separated as yellowish white crystals, yield 59%. It decomposes above 120°C. Found: C, 51.5; H, 5.1. $C_{35}H_{43}AgMoO_5P_2$ calcd.: C, 51.9; H, 5.4%.

The following were prepared analogously:

[Ag(PCy$_3$)(μ-PPh$_2$)Cr(CO)$_5$] dec. 129°C. Found: C, 54.6; H, 6.4. $C_{35}H_{43}AgCrO_5P$ calcd.: C, 54.9; H, 5.7%.

[Ag(PCy$_3$)(μ-PPh$_2$)W(CO)$_5$] dec. 110°C. Found: C, 47.1; H, 5.7. $C_{35}H_{43}AgO_5P_2W$ calcd.: C, 46.8; H, 4.8%.

Results and discussion

Pentacarbonyldiphenylphosphinechromium $Cr(CO)_5PPh_2H$ is readily deprotonated in the presence of silver(I)trifluoromethanesulfonate in diethylamine/toluene solution to yield the new dinuclear phosphido-bridged compound I, as in eq. 1:

$$\mathrm{Cr(CO)_5PPh_2H + AgO_3SCF_3 + Et_2NH \rightarrow \underset{(I)}{AgPPh_2Cr(CO)_5} + NEt_2H_2O_3SCF_3} \tag{1}$$

The coordination sphere of Ag is thought to be completed by Et_2NH molecules. $Mo(CO)_5PPh_2H$ and $W(CO)_5PPh_2H$ react similarly, to give $[Ag(\mu\text{-}PPh_2)M(CO)_5]$ (M = Mo, W). The reactions are complete within a few minutes at ambient temperature. The analogous reaction involving $Cr(CO)_5PCy_2H$ takes one week, and by-products are formed. This reaction complete within 1 d if one equivalent of sodium methoxide is present.

The structures of $[Ag(\mu\text{-}PR_2)M(CO)_5]$ are revealed by $^{31}P\{^1H\}$ NMR spectroscopy which shows the phosphorus atoms to be coupled to ^{107}Ag (52%, $I = \frac{1}{2}$) and ^{109}Ag (48%, $I = \frac{1}{2}$). The Ag–P bonds are kinetically stable on the NMR time scale at temperatures below 273 K. The ^{31}P resonance of phosphido groups is particularly sensitive to the presence of a metal–metal interaction between the bridged metal atoms [4]. The position of the ^{31}P chemical shift indicates the absence of a Ag-Group

TABLE 1

NMR PARAMETERS FOR $[Ag(\mu\text{-}PR_2)M(CO)_5]$ [a]

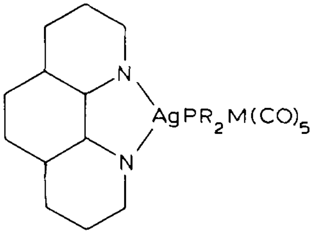
R	M	$\delta(^{31}P)$	$^1J(^{107}Ag,^{31}P)$	$^1J(^{183}W,^{31}P)$
Ph	Cr	1.6	503	–
Ph	Mo	–21.1	477	–
Ph	W	–40.3	496	155
Cy	Cr	19.6	485	–

[a] 0.3 mmol/cm^3 diethylamine/toluene (2/1), 273 K, chemical shifts in ppm to high frequency of 85% H_3PO_4, coupling constants in Hz.

VIB metal interaction in the present compounds. The ^{31}P chemical shifts of the complexes appear at lower frequencies than those for $M(CO)_5PR_2H$, but at higher frequencies than those for $M(CO)_5PR_2^-$ (e.g. $Cr(CO)_5PPh_2Li$: $\delta(^{31}P)$ –30.0 ppm in THF.) The one-bond silver phosphorus coupling constants are smaller than those for the corresponding phosphito, phosphino or phosphine complexes. Electronegative substitution at the phosphorus atom causes an increase in $^1J(Ag,P)$, as reported for $^1J(Pt,P)$ in platinum complexes [5]. The magnitudes of the Ag–P coupling constants of $[Ag(\mu\text{-}PPh_2)M(CO)_5]$ decrease in the order M = Cr > W > Mo, whereas an order of Mo > Cr > W was observed [6] for $J(Sn,P)$ in the series $[Me_3Sn(\mu\text{-}Bu_2P)M(CO)_5]$. The Hg–P couplings in $[Hg\{(\mu\text{-}PPh_2)M(CO)_5\}_2]$ and $[Hg(phen)\{(\mu\text{-}PPh_2)M(CO)_5\}_2]$ are known to decrease in the order W > Cr > Mo [7,8].

Substitution of the P-bound proton in $M(CO)_5PR_2H$ by silver drastically lowers $^1J(^{183}W,^{31}P)$ (from 229 to 155 Hz), as observed for Sn and Hg [6–8].

The NMR data for the compounds in diethylamine/toluene solution are summarized in Table 1. No diethylamine complexes could be isolated in the solid state. The 1,10-phenanthroline complexes II were obtained as stable pale yellow crystals upon addition of one equivalent 1,10-phenanthroline .



(II)

The addition of one equivalent tricyclohexylphosphine to a solution of I in diethylamine/toluene gave the isolable phosphine coordination products III. The nature of these compounds was determined by ^{31}P NMR spectroscopy (see in Table 2).

$Cy_3PAgPR_2M(CO)_5$

(III)

TABLE 2

NMR PARAMETERS FOR $[Ag(PCy_3)(\mu\text{-}PPh_2)M(CO)_5]$ [a]

M	$\delta(PCy_3)$	$\delta(PPh_2)$	$^1J(^{107}Ag, PCy_3)$	$^1J(^{107}Ag, PPh_2)$	$^2J(^{31}P, ^{31}P)$
Cr	36.4(28.3)	1.4(−8.1)	470(399)	459(362)	148(113)
Mo	36.6(28.1)	−18.3(−24.9)	455(396)	429(355)	148(113)
W	36.3(27.6)	−37.2(−43.1)	463(399	440(355)	152(113)

[a] 0.3 mmol/cm^3 CH_2Cl_2, (Et_2NH/MePh = 1/2), 213 K, chemical shifts in ppm to high frequency of 85% H_3PO_4, coupling constants in Hz.

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