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MOLYBDENUM- AND TUNGSTEN-CYCLOPENTADIENYL CARBONYL COMPLEXES WITH HETERO-ALLYL DERIVATIVES AS LIGAND

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Summary

The functionally substituted phosphines LH = $Ph_2PC(X)N(H)R$ (X = S, R = Ph, Me; X = O, R = Ph; X = N-*p*-tol, R = *p*-tol) behave as neutral monodentate (LH) ligands in substitution reactions with $M(CO)_3(\eta^5\text{-}C_5H_5)Cl$ (M = Mo, W), forming $M(CO)_2(\eta^5\text{-}C_5H_5)Cl(LH)$ with P bonded to the metal atom. Deprotonation under the influence of the base Et_3N occurs only in the case of X = S and the chelate complexes $M(CO)_2(\eta^5\text{-}C_5H_5)(L^-)$ are formed with coordination via P and S. The related ligand $Me_2NC(S)N(H)R$ (R = Me, Ph) reacts in the presence of Et_3N to form $M(CO)_2(\eta^5\text{-}C_5H_5)(L^-)$ (M = Mo, W; L^- = $Me_2NC(S)NR^-$; R Me, Ph) with coordination via S and N. Tetramethyldithiobiuret ($Me_2NC(S)$-$N(H)C(S)NMe_2$) reacts with $Mo(CO)_3(\eta^5\text{-}C_5H_5)Cl$ only when Et_3N is present and a complex with a six-membered ring is formed. The molybdenum complexes were prepared by thermal reactions while the tungsten complexes were also prepared photochemically. The complexes were characterised by means of elemental analysis, infrared spectroscopy, and ^1H and $^{31}P[^1H]$ NMR spectroscopy.

Introduction

Ph_2PH reacts with heteroallene molecules to give heteroallyl-type compounds as shown in Fig. 1.

The non-deprotonated compounds (a) can coordinate to transition metals as ordinary tertiary arylphosphines. After deprotonation the ligands (b) coordinate bidentate to transition metals, forming a four-membered ring system resembling dithiocarbamate, xanthate or thioxanthate. The ligands are coordinated through phosphorus and the heteroatom X in known Rh and Ir complexes for X = S, O, NR [1,2] and in Mo complexes for X = S [3]. One example is known in which the deprotonated ligand with X = S is coordinated through P and S as

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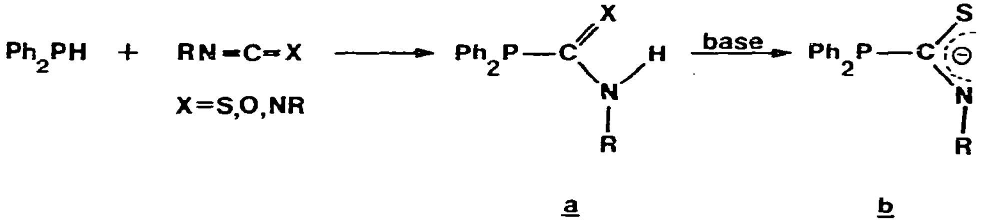


Fig. 1. Preparation of the phosphine-containing ligands.

well as through the nitrogen atom, forming a bridge between two metal atoms [3,4].

In Figure 2 another type of heteroallyl-like ligand is shown. Several Rh, Ir, Pt, Mn, Mo and W [1,4—7] complexes of these thiourea derivatives are known. When R = Me, Ph the thioureido ligand coordinates bidentate through N and S to transition metals to form a four-membered ring system. In the case of R = -C(S)NMe$_2$ (dithiobiuretato) the ligand forms a six-membered ring and is coordinated through both sulfur atoms. In this paper we describe the preparation and properties of Mo and W cyclopentadienyl carbonyl complexes with the neutral phosphine-containing ligands (Fig. 1: a), the deprotonated phosphine-containing ligands (Fig. 1: b), or one of the thiourea derivatives (Fig. 2).

Experimental

IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker WH-90 spectrometer at 90 MHz, while the ^{31}P[^{1}H] NMR spectra were recorded on a Varian XL-100 FT spectrometer at 40.5 MHz. Elemental analyses were performed by the microanalytical department of this University.

All preparations were carried out under nitrogen using Schlenk apparatus. $M(CO)_3(\eta^5\text{-}C_5H_5)Cl$ (M = Mo, W) [8], $Ph_2PC(S)N(H)R$ (R = Ph [9], R = Me [10]), $Ph_2PC(O)N(H)Ph$ [11], $Ph_2PC(N\text{-}p\text{-tol})N(H)p\text{-tol}$ [12], $Me_2NC(S)N(H)R$ (R = Me, Ph) [13] and $Me_2NC(S)N(H)C(S)NMe_2$ [14], were prepared as described in the references cited.

$Mo(CO)_2(\eta^5\text{-}C_5H_5)Cl(LH)$ (Type A). LH = $Ph_2PC(S)N(H)Ph$ (Ia), $Ph_2PC(S)\text{-}N(H)Me$ (IIa), $Ph_2PC(O)N(H)Ph$ (IIIa), $Ph_2PC(N\text{-}p\text{-tol})N(H)p\text{-tol}$ (IVa)

1 mmol of $Mo(CO)_3(\eta^5\text{-}C_5H_5)Cl$ and an equimolar quantity of the appropri-

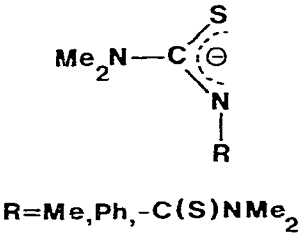


Fig. 2. Structure of the heteroallyl-like thiourea derivative.

ate ligand were refluxed in 15 ml of benzene for two hours. The solvent was removed under reduced pressure. Ia and IIIa were chromatographed on silica with CH_2Cl_2 as eluent. The products were recrystallized from a CH_2Cl_2/n-hexane mixture. Yields about 70%.

Mo(CO)$_2$(η^5-C$_5$H$_5$)(L$^-$) (Type B). L$^-$ = Ph$_2$PC(S)NPh$^-$ (Va), Ph$_2$PC(S)NMe$^-$ (VIa), Me$_2$NC(S)NPh$^-$ (VIIa), Me$_2$NC(S)NMe$^-$ (VIIIa), Me$_2$NC(S)NC(S)NMe$_2^-$ (IX)

1 mmol of $Mo(CO)_3(\eta^5\text{-}C_5H_5)Cl$ and a stoichiometric amount of the appropriate ligand were refluxed in 15 ml of benzene for two hours in the presence of an excess Et_3N. Et_3NHCl was filtered off and after evaporation of the solvent under reduced pressure the mixture was chromatographed on silica with CH_2Cl_2 as eluent. The products were recrystallized from a CH_2Cl_2/n-hexane mixture. Yields about 70%.

W(CO)$_2$(η^5-C$_5$H$_5$)Cl(LH) (Type A). LH = Ph$_2$PC(S)N(H)Ph (Ib), Ph$_2$PC(S)N(H)-Me (IIb), Ph$_2$PC(O)N(H)Ph (IIIb), Ph$_2$PC(N-p-tol)N(H)p-tol (IVb)

a) Thermal reaction. To a solution of 1 mmol $W(CO)_2(\eta^5\text{-}C_5H_5)Cl$ in 15 ml of benzene an equimolar quantity of the appropriate ligand was added. The mixture was refluxed until $W(CO)_3(\eta^5\text{-}C_5H_5)Cl$ was no longer detectable by IR spectroscopy. The solvent was removed under reduced pressure. In the case of LH = $Ph_2PC(S)N(H)Ph$, chromatography on a silica column with CH_2Cl_2 as eluent was necessary. The products were recrystallized from a benzene/petroleum ether (60—80) mixture. Yield approximately 50%.

b) Photochemical reactions. To a solution of 1 mmol $W(CO)_3(\eta^5\text{-}C_5H_5)Cl$ in 125 ml of benzene an equimolar quantity of the ligand was added. The mixture was irradiated for 16 hours with light of 300—350 nm. The work up was the same as above. The yields were very low owing to the formation of much $[W(CO)_3(\eta^5\text{-}C_5H_5)]_2$.

W(CO)$_2$(η^5-C$_5$H$_5$)(L$^-$) (Type B). L$^-$ = Ph$_2$PC(S)NPh$^-$ (Vb), Ph$_2$PC(S)NMe$^-$ (VIb), Me$_2$NC(S)NPh$^-$ (VIIb), Me$_2$NC(S)NMe$^-$ (VIIIb)

a) Thermal reaction. To a solution of 1 mmol $W(CO)_3(\eta^5\text{-}C_5H_5)Cl$ in 15 ml of benzene an equimolar quantity of the appropriate ligand and an excess of Et_3N was added. The mixture was refluxed for 4 hours and Et_3NHCl was filtered off. The benzene was removed under reduced pressure. Vb was chromatographed on silica with CH_2Cl_2 as eluent and recrystallized from a CH_2Cl_2/n-hexane mixture. VIb, VIIb and VIIIb were recrystallized from a benzene/n-hexane mixture. Yields approximately 50%.

b) Photochemical reactions. To a solution of 1 mmol $W(CO)_3(\eta^5\text{-}C_5H_5)Cl$ in 125 ml benzene an equimolar quantity of the ligand and an excess of Et_3N were added. The mixture was irradiated for 16 hours with light of 300—350 nm. The work up was as in the case of the thermal reaction. The yields were lower (10—25% owing to the formation of $[W(CO)_3(\eta^5\text{-}C_5H_5)]_2$).

Results and discussion

Reactions and products

The reactions of $M(CO)_3(\eta^5\text{-}C_5H_5)Cl$ (M = Mo, W) with $Ph_2PC(X)N(H)R$ (X =

TABLE 1

ELEMENTAL ANALYSES (CALCULATED VALUES IN PARENTHESES)

No.	Compound	C(%)	H(%)	N(%)
Ia	$Mo(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2PC(S)N(H)Ph)Cl$	53.78	3.66	2.47
		(54.42)	(3.69)	(2.44)
Ib	$W(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2PC(S)N(H)Ph)Cl$	47.07	3.27	2.14
		(47.07)	(3.17)	(2.12)
IIa	$Mo(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2PC(S)N(H)Me)Cl$	49.80	3.82	2.58
		(49.28)	(3.74)	(2.74)
IIb	$W(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2PC(S)N(H)Me)Cl$	42.51	3.24	2.38
		(42.06)	(3.19)	(2.34)
IIa	$Mo(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2PC(O)N(H)Ph)Cl.C_6H_6$ [a]	60.95	4.60	2.16
		(60.47)	(4.28)	(2.20)
IIIb	$W(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2PC(O)N(H)Ph)Cl.C_6H_6$ [a]	52.85	3.66	1.89
		(53.10)	(3.76)	(1.94)
IVa	$Mo(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2PC(N\text{-}p\text{-tol})N(H)p\text{-tol})Cl.CH_2Cl_2$ [a]	56.99	4.43	3.81
		(56.34)	(4.32)	(3.75)
IVb	$W(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2PC(N\text{-}p\text{-tol})N(H)p\text{-tol})Cl$ [b]	57.88	4.56	3.90
		(54.53)	(4.04)	(3.74)
Va	$Mo(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2PC(S)NPh)$	57.42	3.62	2.52
		(58.11)	(3.75)	(2.61)
Vb	$W(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2PC(S)NPh)$	50.17	3.20	2.23
		(49.92)	(3.20)	(2.24)
VIa	$Mo(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2PC(S)NMe)$	53.19	4.02	2.95
		(53.06)	(3.82)	(2.94)
VIb	$W(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2PC(S)NMe)$	44.31	3.30	2.41
		(44.76)	(3.20)	(2.48)
VIIa	$Mo(CO)_2(\eta^5\text{-}C_5H_5)(Me_2NC(S)NPh)$	48.32	4.26	7.00
		(48.48)	(4.07)	(7.07)
VIIb	$W(CO)_2(\eta^5\text{-}C_5H_5)(Me_2NC(S)NPh)$	37.30	3.14	5.50
		(39.67)	(3.30)	(5.78)
VIIIa	$Mo(CO)_2(\eta^5\text{-}C_5H_5)(Me_2NC(S)NMe)$ [c]	—	—	—
VIIIb	$W(CO)_2(\eta^5\text{-}C_5H_5)(Me_2NC(S)NMe)$	31.16	3.32	6.69
		(31.28)	(3.32)	(6.64)
IX	$Mo(CO)_2(\eta^5\text{-}C_5H_5)(Me_2NC(S)NC(S)NMe_2)$	38.34	4.32	10.23
		(38.33)	(4.21)	(10.32)

[a] The presence of the solvent molecule was confirmed by ^1H NMR spectroscopy. [b] From the crude reaction product it is impossible to remove small amounts of the free ligand. [c] No reliable elemental analysis could be done because the compound decomposes upon recrystallization.

S, R = Me, Ph; X = O, R = Ph; X = N-*p*-tol, R = *p*-tol) yield two types of products: Type A: Complexes in which one carbonyl group is replaced by the neutral ligand. Type B: Complexes in which one carbonyl group and the chlorine are replaced by the deprotonated ligand.

In the case of X = O and X = N-*p*-tol only type A complexes can be prepared. The thiourea derivatives $Me_2NC(S)N(H)R$ (R = Me, Ph, $-C(S)NMe_2$) give products with $M(CO)_3(\eta^5\text{-}C_5H_5)Cl$ (M = Mo, W) only when Et_3N is present. In these cases it is impossible to prepare type A complexes and only type B complexes are obtained. When R = $-C(S)NMe_2$ only a Mo complex can be prepared. The reactions of the metal complexes with $Ph_2PC(S)N(H)R$ (R = Me, Ph) yield either type A or type B complexes depending upon whether or not Et_3N is added to the reaction mixture.

The molybdenum complexes are prepared in refluxing benzene, while the tungsten complexes can be prepared in refluxing benzene or by irradiation with

TABLE 2

INFRARED SPECTRAL DATA [a]

No.	ν(CO)(cm^{-1})				Solvent	Ligand vibrations in CsI-pellets (cm^{-1})								ν(M—Cl) (cm^{-1})
Ia	1979vs		1898s		CH_2Cl_2		1555s	1495s					975m	262
Ib		1962vs		1876s	CH_2Cl_2		1556s	1489m						266
IIa	1977vs		1894s		CH_2Cl_2		1539m		1360s				958m	268
IIb		1970vs		1879s	C_6H_6		1538s		1360s				940s	275
IIIa	1979vs		1896s		CH_2Cl_2	1662s	1542s							266
IIIb		1962vs		1874s	C_6H_6	1666s	1548s							266
IVa	1975vs		1890s		CH_2Cl_2		1626m	1514s						271
IVb		1956vs		1874s	C_6H_6		1626m	1512s						268
Va	1960vs		1885s		CH_2Cl_2		1552s						908m	—
Vb		1948vs		1862s	CH_2Cl_2		1557m						914m	—
VIa	1972vs		1887s		CH_2Cl_2		1575m						900m	—
VIb		1948vs		1860	CH_2Cl_2		1582s						904	—
VIIa	1947vs		1847s		CH_2Cl_2		1545s		1357s	1198s	1107s	955w	788m	—
VIIb		1936vs		1834s	C_6H_6		1546s		1360s	1202s	1108s	958w	796m	—
VIIIa	1946vs		1845s		CH_2Cl_2		1570s		1348s	1247m	1124s		805s	—
VIIIb		1936vs		1836s	C_6H_6		1572s		1350s	1248m	1127s	818s	808s	—
IX	1950vs		1853s		CH_2Cl_2		1598s		1358s	1308s	1132s		902s	—

[a] Vibration frequencies (ν) and relative intensities (vs = very strong, s = strong, m = medium and w = weak).

light of 300—350 nm. The yields of the tungsten complexes are lower than those of the molybdenum complexes (50 vs 70%).

Characterization of the type A complexes $M(CO)_2(\eta^5\text{-}C_5H_5)(LH)Cl$. LH = $Ph_2PC(X)N(H)R$ (X = S, R = Ph, Me; X = O, R = Ph; X = N-p-tol, R = p-tol)

The reactions of $M(CO)_3(\eta^5\text{-}C_5H_5)Cl$ with $Ph_2PC(X)N(H)R$ yield products which all analyse according to $M(CO)_2Cl(\eta^5\text{-}C_5H_5)(LH)$. In the infrared spectra of solutions of these compounds (for solvent see Table 2) two carbonyl stretching frequencies can be seen. The carbonyl stretching frequencies of the tungsten complexes are lower than those of the molybdenum complexes, this is due to the stronger electron releasing properties of tungsten compared with molybdenum. Among these compounds there is no significant difference in CO frequencies, which means that the heteroatom X has no influence. The both CO groups are in *cis* positions, as can be concluded from the infrared spectra and from the ^{1}H NMR spectra. In the infrared spectra the signal at highest frequency has the highest intensity. Manning [15] has suggested that in these cases the CO groups are in *cis* positions. In the proton NMR spectra of $M(CO)_2(\eta^5\text{-}C_5H_5)ClL$, where L is a phosphine or phosphite, a doublet is found for the C_5H_5 proton when the both CO groups are in *trans* positions and a singlet when the CO groups are in *cis* position [15,16]. Thus the NMR data, shown in Table 3, confirm the conclusion that in these type A complexes the both CO groups are in *cis* positions. In the infrared spectra the ν(M—Cl) is found at about 268 cm^{-1}, which is lower than the value for the starting complex. This is due to the better π-acceptor properties of the carbonyl group compared to the phosphine-containing ligand.

All compounds of type A show a broad signal in the ^{1}H NMR spectra due to the N—H proton.

TABLE 3

^{1}H NMR SPECTRAL DATA [a,b]

No.	δ(-N—H) [c]	δ(-C_5H_5)	δ(-CH_3)		Solvent
Ia	11.86	5.60	—		CD_2Cl_2
Ib	11.48	5.75	—		CD_2Cl_2
IIa	9.95	5.55	3.26d	3.20d [d]	CD_2Cl_2
IIb	9.56	5.70	3.27d	3.22d	CD_2Cl_2
IIIa	10.12	5.55	—		CD_2Cl_2
IIIb	10.08	5.15	—		C_6D_6
IVa	8.26	5.56	2.18		CD_2Cl_2
IVb		5.13	1.89		C_6D_6
Va		5.31	—		CD_2Cl_2
Vb		5.33	—		C_6D_6
VIa		5.31	3.29	3.26	CD_2Cl_2
VIb		5.41	3.26	3.23	CD_2Cl_2
VIIa		5.49	2.35		CD_2Cl_2
VIIb		5.21	2.16		C_6D_6
VIIIa		5.53	NMe : 3.20	NMe_2 : 2.85	CD_2Cl_2
VIIIb		5.68	NMe : 3.24	NMe_2 : 2.85	CD_2Cl_2
IX		5.38	3.47	3.22	CD_2Cl_2

[a] δ-values in ppm relative to tetramethylsilane (internal standard). [b] All signals are singlet unless otherwise stated. [c] All these signals are broad. [d] d = doublet.

In the ^1H NMR spectra of $M(CO)_2(\eta^5\text{-}C_5H_5)Cl[Ph_2PC(S)N(H)Me]$ (M = Mo, W) the methyl protons show a doublet of doublets. There is coupling of the CH_3 protons with the N—H proton, which is proven by decoupling experiments (^3J(H—H) = 5 Hz). The small coupling constant of 1.17 Hz probably arises from a ^4J coupling of the CH_3 protons with the phosphorus atom.

In the $^{31}P[^1H]$ NMR spectra (Table 4) the phosphine shows a considerable downfield shift upon coordination. The Δ-values ($\Delta = \delta_{compl} - \delta_{free\ ligand}$) of the molybdenum complexes are more negative than those of the tungsten complexes. This phenomenon was also observed by Garrou [17] in Mo^0 and W^0 complexes. The downfield shift is caused, inter alia, by the net electron donation of the phosphorus atom upon coordination. Grimm et al [18] and George [19] suggest that large coordination shifts will be observed for good σ-donor groups and small shifts for good π-acceptor groups. This implied that the $Ph_2PC(S)N(H)R$ ligands are the better σ-donors and the $Ph_2PC(O)N(H)Ph$ and $Ph_2PC(N\text{-}p\text{-tol})N(H)p\text{-tol}$ ligands are the better π-acceptors, which can be attributed to the greater electronegativity of the O and N-*p*-tol groups. However, this trend is not reflected in the ν(CO) in the infrared spectra or in the $^{183}W—^{31}P$ coupling constants in the $^{31}P[^1H]$ NMR spectra of the tungsten complexes. For all these type A complexes a $^1J(^{183}W—^{31}P)$ value of 260 Hz is found. All the data suggest that in $M(CO)_2(\eta^5\text{-}C_5H_5)Cl(LH)$ the protonated ligand is bonded monodentate through P to the metal, with the M—Cl bond remaining intact, and that the carbonyl group replaced by the phosphine-containing ligand.

Characterization of the type B complexes: $M(CO)_2(\eta^5\text{-}C_5H_5)(L^-)$ *(*L^- *=* $[Ph_2PC(S)NR]^-$ *and* $[Me_2NC(S)NR]^-$ *(R = Ph, Me), M = Mo, W; L =* $[Me_2NC(S)\text{-}NC(S)NMe_2]^-$*, M = Mo)*

$L^- = [Ph_2PC(S)NR]^-$ (R = Me, Ph). When Et_3N is present in the reaction of $M(CO)_2(\eta^5\text{-}C_5H_5)Cl$ (M = Mo, W) with $Ph_2PC(S)N(H)R$ the N—H bond is broken and a chelate ring is formed. In Figure 3 a reaction scheme for these reactions is given. In the infrared spectra of a solution of these complexes (for solvent see Table 2) two carbonyl stretching bands are found, of which the band at highest

TABLE 4

$^{31}P[^1H]$ NMR SPECTRAL DATA [a]

No.	$\delta_{free\ ligand}$	$\delta_{complex}$	Δ [b]	$J(^{183}W—^{31}P)$ (Hz)
Ia	—17.16	—69.78	—52.62	—
Ib	—17.16	—44.39	—27.23	260
IIa	—12.52	—65.15	—52.63	—
IIb	—12.52	—40.12	—27.60	261
IIIa	—10.96	—53.18	—42.22	—
IIIb	—10.96	—26.03	—15.07	260
IVa	—14.73	—54.17	—39.44	—
IVb	—14.73	—25.55	—10.82	262
Va	—17.16	—24.81	—7.65	—
Vb	—17.16	—2.33	+14.83	230
VIa	—12.52	—24.49	—11.97	—
VIb	—12.52	—2.03	+10.49	231

[a] δ-values in ppm relative to $O=P(OMe)_3$ for compounds in C_6D_6 solution using the solvent as internal lock; upfield is positive. [b] $\Delta = \delta_{complex} - \delta_{free\ ligand}$.

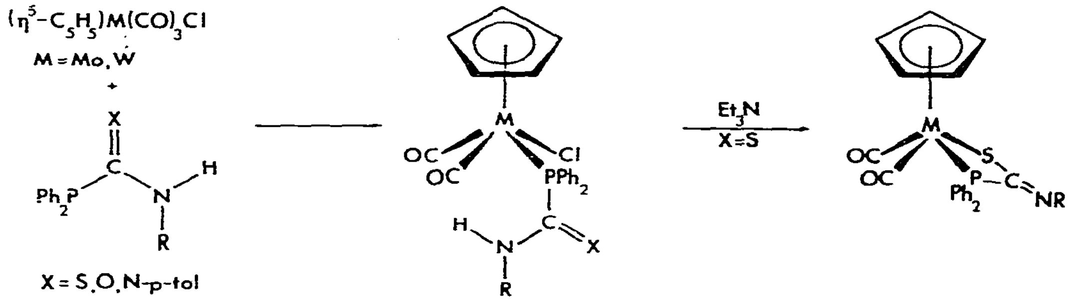


Fig. 3. Reactions of $M(CO)_3(\eta^5\text{-}C_5H_5)$ (M = Mo, W) with the phosphine-containing ligands.

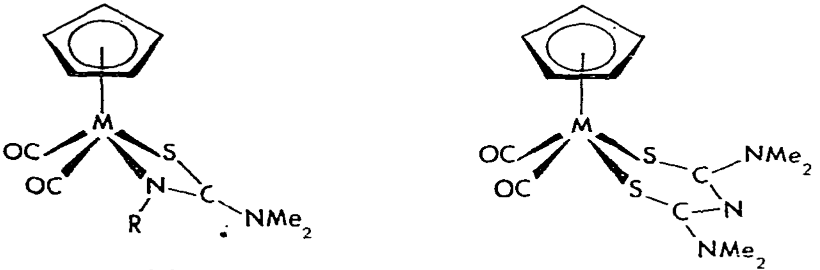
frequency is also of highest intensity, as observed for type A compounds, so we conclude that the carbonyl groups are again in *cis* position. The ligand vibrations in the IR spectra of these type B compounds are similar to those of Rh complexes of $Ph_2PC(S)NPh^-$ [2], in which P, S coordination was assumed. There is also a lowering of the C=S stretching frequency to about 910 cm^{-1}. The ν(CN) of the compounds with R = Ph are lower than those of the analogous complexes with R = Me owing to the electron-withdrawing effect of the phenyl group.

In the proton NMR spectra of $M(CO)_2(\eta^5\text{-}C_5H_5)[Ph_2PC(S)NMe]$ the CH_3 protons show two singlets. We think that two rotamers are present because of hindrance to rotation around the C—N bond. There is no coupling between the P atom and the CH_3 protons. In the $^{31}P[^1H]$ NMR spectra an upfield shift relative to the comparable type A complexes is observed of about 40 ppm. The $^1J(^{183}W—^{31}P)$ values are about 230 Hz, lower than the value (260 Hz) found for the type A compounds.

The difference in chemical shift between the monodentate coordinated $Ph_2PC(S)N(H)R$ and the bidentate coordinated $Ph_2PC(S)NR^-$ is about 40 ppm. A difference in chemical shift between phosphorus atoms incorporated in a four-membered ring and those not incorporated in a four-membered ring was also noted by Garrou [17].

$L^- = Me_2NC(S)NR^-$ (R = Ph, Me, $\text{-}C(S)NMe_2$). The infrared spectra show again that the CO groups are in *cis* positions. The CO frequencies of the thioureido complexes are 20—40 cm^{-1} lower than those of the comparable complexes with $Ph_2PC(S)NR^-$ as bidentate ligand. This can be ascribed to the better electron donating properties of the thioureido ligand compared the phosphine-containing ligand. Comparison of the ligand vibrations in the IR spectra of the thioureido complexes with known Rh^I and Rh^{III} complexes suggest that these ligands are coordinated through nitrogen and sulfur. Coordination through nitrogen and sulfur in a Rh^{III} complex has been confirmed by an X-ray structure determination [20]. The dithiobiuretato ligand (R = $\text{-}C(S)NMe_2$) is coordinated through both the sulfur atoms, as can be seen by comparison of the infrared spectrum with those of Rh^I complexes for which S,S-coordination is reasonably sure.

The ^1H NMR spectra of the thioureido complexes show only one signal for



M=Mo,W M=Mo

Fig. 4. Probable structures of $M(CO)_2(\eta^5\text{-}C_5H_5)(Me_2NC(S)NR)$ (M = Mo, W; R = Ph, Me) and $Mo(CO)_2\text{-}(\eta^5\text{-}C_5H_5)(Me_2NC(S)NC(S)NMe_2)$.

the NMe_2 protons, which indicates free rotation around the C—N bond. In the dithiobiuretato complexes there is more double bond character in the CN bond, and this gives rise to two CH_3 signals in the NMR spectrum.

In Figure 4 the probable structures for the thioureido and dithiobiuretato complexes are given.

Conclusions

The observations reported in this article can be summarized as follows. In the reaction with $M(CO)_3(\eta^5\text{-}C_5H_5)Cl$ (M = Mo, W) the phosphine-containing ligands from Fig. 1 resemble tertiary phosphines in their ability to replace a CO group to form a metal—phosphorus bond [21]. On the other hand, Dean and Heyl [22] reported the reaction of xanthate and thioxanthate with $M(CO)_3(\eta^5\text{-}C_5H_5)Cl$ (M = Mo, W) to give $M(CO)_3(\eta^5\text{-}C_5H_5)(L^-)$ and $M(CO)_2\text{-}(\eta^5\text{-}C_5H_5)(L^-)$ ($L^- = S_2COR^-$ or S_2CSR^-). Two reaction pathways are possible: one in which the first step is the displacement of the Cl ligand and one in which the first step is the displacement of the CO group. In the reaction with the phosphine-containing ligand the pathway seems to be that in which the first step is the replacement of a CO. In the case of the thiourea derivatives we think that both pathways are possible, although we found no tricarbonyl products.

From the position of the ν(CO) values of the complexes containing the deprotonated ligands we can conclude that the electron-donating ability of the thioureido ligand is better than that of the deprotonated phosphine-containing ligand. The electron donation by the thioureido ligand seems to be even better than that of the dithiocarbamate ligands (ν(CO) of the Mo-dtc complex: 1954 and 1870 cm^{-1}; ν(CO) of the W-dtc complex: 1943 and 1854 cm^{-1} [23]) so that the order of increasing electron donation is: $Ph_2PC(S)NR^- < S_2CNR_2^- < RNC(S)NR_2^-$. The same order, as indicated by the CO stretching frequencies or the number of CO groups, is found in $Rh^I(CO)(PPh_3)(L^-)_2$ and $Mo^{II}(CO)_{2,3}\text{-}(L^-)_2$ complexes [3,24]. Finally, in the reaction of the ligands used with Rh^I, Ir^I and Pt^0 phosphine complexes a spontaneous breaking of the N—H bond has sometimes been observed. In the reactions of these ligands with molybdenum and tungsten cyclopentadienyl carbonyl complexes described above such a process was never observed, and use of the base Et_3N was necessary.

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