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Synthesis and characterization of a series of *trans*-[$(CO)_5M\{Ph_2PX(CH_2)_3N{=}CHC_6H_4$-*o*-O}]$_2$M′ (M = Mo; X = NH or M = Cr, W; X = CH_2; M′ = Ni, Cu, Zn) complexes and the X-ray crystal structure of *trans*-[$(CO)_5Mo\{P(OCH_2CMe_2CH_2O)NH(CH_2)_2$-$N{=}CHC_6H_4$-*o*-O}]$_2$Cu

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Abstract

A series of heterotrinuclear complexes of the type *trans*-[$(CO)_5M$-$\{Ph_2PX(CH_2)_3N{=}CHC_6H_4$-*o*-O}]$_2$M′ (M = Mo; X = NH; M′ = Ni, Cu or M = Cr, W; X = CH_2; M′ = Ni, Cu, Zn) have been synthesized either by the reactions of coordinated P-donor ligands (X = NH) or by the sequential reactions of the metals with the free ligands (X = CH_2). Spectroscopic studies of the complexes (IR, UV-VIS and multinuclear NMR) indicate that their solution conformations are quite different from those of the previously studied *trans*-[$(CO)_5Mo\{R_2PNH(CH_2)_2N{=}CHC_6$-$H_4$-*o*-O}]$_2$M′ ($R_2 = OCH_2CMe_2CH_2O$, Ph_2; M′ = Ni, Cu) complexes. These studies also indicate that the coordination geometries of Ni^{2+} and Zn^{2+} in these complexes are different. The Ni^{2+} ion is in a square planar coordination environment while the coordination geometry of the Zn^{2+} is most likely tetrahedral.

The molecular structure of *trans*-[$(CO)_5Mo\{P(OCH_2CMe_2CH_2O)NH(CH_2)_2$-$N{=}CHC_6H_4$-*o*-O}]$_2$Cu has been determined. The complex crystallizes from a THF-methanol mixture in the triclinic space group $P\bar{1}$ (crystal data: *a* 6.613(2), 9.725(4), *c* 18.725(7) Å; α 93.65(3), β 99.07(4), γ 102.85(4); $Z = 1$). The Cu^{2+} is coordinated to two *o*-salicylaldiminate groups in a *trans* square planar geometry, and the Mo is coordinated to five carbonyls and a P-donor group in a distorted octahedral geometry. The conformation of the bridging group in the complex is very different from that observed in other heterotrinuclear complexes due to the lack of phenyl-bis(*o*-salicylaldiminato)metal stacking interactions.

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Introduction

Incorporation of a hard metal center into the ligand framework of a soft mononuclear transition metal catalyst may greatly alter the activity and selectivity of the catalyst. This has recently been demonstrated using bimetallic Rh–Zr and Rh–Ti complexes as alkene hydroformylation catalysts [1–4]. Thus, there is considerable interest in the preparation and coordination chemistry of ligands capable of coordination to both soft and hard metal centers.

Ligands that may be particularly useful in this regard are those containing at least one P-donor site and also multiple N- and/or O-donor sites. P-donor ligands are found in many mononuclear, catalytically active, transition metal complexes [5]. Multiple N- and O-donor sites are excellent for the coordination of hard metal cations. Ligands of this type include P-donor-crown ethers and -crown aminoethers [6–12], phosphine-carboxylates [13], phosphine-diketonates [14–16] and P-donor-*o*-salicylaldiminates [17–20].

We have been involved in a study of the coordination chemistry of P-donor-*o*-salicylaldiminates. These ligands are of interest because both the number of bridging ligands and the nature of the P substituents have significant effects upon the solution and solid state conformations of the complexes [19,20]. In this paper, we report the synthesis and spectroscopic characterization of a series of heterotrinuclear complexes of the type *trans*-$[(CO)_5M\{Ph_2PX(CH_2)_3N{=}CHC_6H_4\text{-}o\text{-}O\}]_2M'$ (M = Mo; X = NH; M′ = Ni, Cu or M = Cr, W; X = CH_2; M′ = Ni, Cu, Zn). The spectroscopic data of these complexes are compared to those of the previously reported *trans*-$[(CO)_5Mo\{R_2PNH(CH_2)_2N{=}CHC_6H_4\text{-}o\text{-}O\}]_2M'$ (R_2 = $OCH_2CMe_2CH_2O$, Ph_2; M′ = Ni, Cu) complexes in order to understand the effects of variations in the length of the bridging group upon the conformations of the complexes. In addition, the X-ray crystal structure of the previously prepared $[(CO)_5Mo\{P(OCH_2CMe_2CH_2O)NHCH_2CH_2N{=}CHC_6H_4\text{-}o\text{-}O\}]_2Cu$ [20] has been determined, and the conformation of this complex is discussed in view of the results of the spectroscopic studies.

Experimental

All reactions were carried out under dry N_2. Both tetrahydrofuran (THF) and diethyl ether were distilled from benzophenone sodium. Other solvents were used as received. Diphenylphosphine (Pressure) was distilled before use. Triethylamine and 1,3-diaminopropane were distilled from calcium hydride before use. $Mo(CO)_5(Ph_2PCl)$ [21] and $M(CO)_5(CH_3CN)$ (M = Cr, W) [22] were prepared by literature methods.

Multinuclear NMR spectra of 0.10 *M* chloroform-d_1 solutions of all diamagnetic complexes were taken on a GE NT-300 wide-bore multinuclear NMR spectrometer. Proton NMR spectra of chloroform-d_1 solutions of the ligands were taken on a Varian 360L NMR spectrometer. Infrared spectra of dilute dichloromethane solutions of the complexes in the 2100–1800 cm^{-1} region and of KBr disks of the complexes were run on a Perkin Elmer 283B infrared spectrometer. Mass spectra were run on a Hewlett Packard 5985 GC-MS using an unheated, direct insertion probe. The NMR and IR spectroscopic data are summarized in Tables 1, 2 and 3.

Table 1

^{13}C NMR spectroscopic data for the $C{\equiv}O$ and salicylaldiminato groups

complex	*trans* $C{\equiv}O$ [a]		*cis* $C{\equiv}O$ [a]		$C{=}N$ [b]	$C{-}O$ [b]
	$\delta(^{13}C)$ (ppm)	$\lvert ^2J(PC)\rvert$ (Hz)	$\delta(^{13}C)$ (ppm)	$\lvert ^2J(PC)\rvert$ (Hz)	$\delta(^{13}C)$ (ppm)	$\delta(^{13}C)$ (ppm)
I	210.49	24	205.65	10		
II	210.25	24	205.56	10	160.96	165.28
III	210.22	24	205.57	9	160.93	164.10
VII					161.68	164.68
IX	221.31	7	216.79	13	161.09	165.01
X			222.70 [c]	13	161.20	164.77
XI	221.30	6	216.79	13	160.61	163.78
XII	221.19	7	216.77	13	170.52	171.20
XIII	199.23	23	196.92	6	161.08	165.04
XIV	199.22	21	196.91	7	160.73	163.80
XVI	199.10	21	196.89	7	170.24	171.20

[a] Doublet. [b] Singlet. [c] Triplet.

$(CO)_5Mo\{Ph_2PNH(CH_2)_3NH_2\}$ (I). A solution of 12.0 g (26.3 mmol) of $Mo(CO)_5(Ph_2Cl)$ in 50 ml of THF was added dropwise to a solution of 12.0 ml (141 mmol) of 1,3-diaminopropane in 20 ml of THF over a 30 min period at ambient temperature. After 1.5 h the solvent was removed. The residue was treated with 150 ml of deionized water, and the mixture was stirred for 18 h. Filtration of the mixture then yielded 12.5 g (96.2 %) of crude I.

$(CO)_5Mo\{Ph_2NH(CH_2)_3N{=}CHC_6H_4\text{-}o\text{-}OH\}$ (II). A solution of 8.00 g (16.2 mmol) of I and 1.76 ml (16.2 mmol) of *o*-salicylaldehyde in 25 ml of methanol was stirred at ambient temperature for two days. The reaction mixture was then evaporated to dryness, and the residue was washed with 20 ml of cold methanol t

Table 2

^{13}C NMR data for the methylene groups

Compound	$\underset{1}{Ph_2P\text{-}X}\ \underset{2}{\text{-}CH_2}\underset{3}{\text{-}CH_2}\underset{4}{\text{-}CH_2}\text{-}N{=}CHC_6H_4\text{-}o\text{-}O$						
	1		2		3		4
	$\delta(^{13}C)$ [a]	$\lvert ^1J(PC)\rvert$	$\delta(^{13}C)$ [a]	$\lvert ^2J(PC)\rvert$	$\delta(^{13}C)$ [a]	$\lvert ^3J(PC)\rvert$	$\delta(^{13}C)$ [b]
I			42.62	8	34.05	2	40.41
II			41.50	8	32.66	2	56.60
III			41.60	7	34.71	3	55.12
VII	23.55	17	27.77	11	32.13	13	59.08
IX	32.08	22	21.45 [b]	–	31.87	9	58.85
X	33.09 [c]	22 [d]	21.40 [b]	–	31.99 [c]	13 [e]	58.85
XI	32.33	22	21.55 [b]	–	34.06	13	57.74
XII	31.71	21	20.96 [b]	–	31.53	13	60.26
XIII	32.80	26	22.09 [b]	–	31.75	14	58.93
XIV	32.98	26	22.11 [b]	–	33.89	14	57.74
XVI	32.36	26	21.56 [b]	–	31.39	14	60.28

[a] Doublet. [b] Singlet. [c] Apparent pentet. [d] $\lvert ^1J(PC)+{}^3J(PC)\rvert$. [e] $\lvert ^2J(PC)+{}^4J(PC)\rvert$.

Table 3

^{31}P NMR and IR data

Complex	$\delta(^{31}P)$ [a] (ppm)	$\nu(CO)$ [b,c]				$\nu(CN)$ [d] (cm^{-1})
		A_1^1 (cm^{-1})	A_1^2 (cm^{-1})	B_1 (cm^{-1})	B_2 (cm^{-1})	
I	75.65	2074m	1947s	1990w	1933sh	–
II	77.88	2074m	1946s	1990w	1932sh	1627m
III	78.18	2074m	1946s	1991w	1932sh	1610m
IV	–	2074m	1946s	1990w	1932sh	1620m
VII	−15.97	–	–	–	–	1632m
VIII	–	–	–	–	–	1618m
IX	46.80	2064m	1940s	1981w	1928sh	1636m
X	62.46		1885s [f]			1636m
XI	46.70	2064m	1940s	1983w	1928sh	1615m
XII	46.59	2062m	1942s	1988w	1930sh	1618m
XIII	9.98	2073m	1938s	1977m	1925sh	1628m
XIV	9.92	2072m	1938s	1982w	1927sh	1613m
XV	–	2073m	1938s	1978m	1928sh	1620m
XVI	9.73	2072m	1938s	1973m	1927sh	1618m

[a] 0.10 *M* $CDCl_3$ solution. [b] m = medium, s = strong, sh = shoulder. [c] Dilute CH_2Cl_2. [d] KBr disk. [e] 0.01 *M* CH_2Cl_2. [f] E_u.

yield 8.25 g of crude II (reaction yield 85.1%). Recrystallization from dichloromethane/hexanes yielded analytically pure, yellow II (m.p. 178.5 °C). Anal. Found: C, 54.02; H, 3.93; N, 4.65. $C_{27}H_{24}MoN_2O_6P$ calcd.: C, 54.21; H, 3.88; N, 4.68%.

$[(CO)_5Mo\{Ph_2NH(CH_2)_3N{=}CHC_6H_4\text{-}o\text{-}O\}]_2Ni$ (III). A solution of 0.336 g (0.92 mmol) of $Ni(ClO_4)_2 \cdot 6H_2O$ in 20 ml of ethanol was slowly added to a solution of 1.00 g (1.67 mmol) of II and 4.60 ml (33.4 mmol) of triethylamine in 20 ml of ethanol. A green precipitate of III began to form immediately. The reaction mixture was stirred for 18 h, and then 1.03 g (100%) of crude III was collected. Recrystallization from dichloromethane/hexanes yielded analytically pure, green III (m.p. 66–70 °C with decomposition). Anal. Found: C, 51.67; H, 3.61; N, 4.41. $C_{54}H_{44}Mo_2N_4NiO_{12}P_2$ calcd.: C, 51.74; H, 3.54; N, 4.47%.

$[(CO)_5Mo\{Ph_2NH(CH_2)_3N{=}CHC_6H_4\text{-}o\text{-}O\}]_2Cu$ (IV). A solution of 1.00 g (1.67 mmol) of II and 0.167 g (0.84 mmol) of $Cu(OAc)_2 \cdot H_2O$ in 20 ml of THF was stirred for 4 days at ambient temperature and then evaporated to dryness to yield 1.05 g (100%) of crude IV as a green-brown powder. Recrystallization from dichloromethane/hexanes yielded analytically pure, green-brown IV (m.p. 122–124 °C). Anal. Found: C, 51.46; H, 3.55; N, 4.43. $C_{54}H_{44}CuMo_2N_4O_{12}P_2$ calcd.: C, 51.56; H, 3.53; N, 4.45%.

$Ph_2P(CH_2)_3CN$ (V). A solution of 1.6 *M* n-BuLi in hexanes (43.3 ml, 67.6 mmol) was added dropwise to a solution of 11.84 ml (67.6 mmol) of Ph_2PH in 130 ml diethyl ether at −78 °C. After 30 min, a solution of 6.80 ml of $Br(CH_2)_3CN$ in 20 ml of degased diethyl ether was added dropwise at −78 °C. The reaction mixture was allowed to warm to ambient temperature after which it was evaporated to dryness. The residue was treated with 120 ml of dichloromethane/hexanes (1/2) and 120 ml of deionized water, and then the organic layer was separated, dried with anhydrous $MgSO_4$ and evaporated to dryness. The residue was vacuum distilled to

yield 12.72 g (74.30%) of V (b.p. 140–150 °C at 0.1 mmHg). (MS, m/z for M^+: 253, 199, 183, 107, 91. ^{1}H NMR (δ, multiplicity, J): Ph (7.25 ppm, 10, multiplet), CH_2CN (2.38 ppm, 2, triplet $|^3J(HH)|$ 7 Hz). $CH_2CH_2CH_2$ (2.10 ppm, 2, multiplet), CH_2P (1.82 ppm, 2, multiplet)}.

$Ph_2P(CH_2)_4NH_2$ (VI). A solution of 12.72 g (50.28 mmol) of V in 25 ml of diethyl ether and 25 ml of THF was added dropwise to a slurry of 2.0 g of $LiAlH_4$ in 75 ml of diethyl ether at 5 °C under N_2. The reaction mixture was stirred at 5 °C for 4 h, and then the excess $LiAlH_4$ was deactivated by carefully adding 35 ml of degassed water and 65 ml of 10% NaOH solution. This mixture was filtered through a 1 cm layer of celite in a medium fritted glass funnel, and the filtrate was evaporated to dryness to yield 12.90 g (99.6%) of crude VI. {^{1}H NMR (δ, multiplicity, J): Ph (7.25 ppm, 10, multiplet), CH_2NH_2 (2.63 ppm, 2, triplet $|^3J(HH)|$ 5 Hz), $CH_2CH_2NH_2$ (2.03 ppm, 2, multiplet), CH_2CH_2P and CH_2CH_2P (1.56 ppm, 4, multiplets), NH_2 (1.15 ppm, 2, broad singlet)}.

$Ph_2P(CH_2)_4N{=}CHC_6H_4$-o-OH (VII). A solution of 15.6 ml (13.6 g, 112 mmol) of *o*-salicylaldehyde was added to a solution of 28.7 g (113 mmol) of VI in 200 ml of ethanol under N_2. The reaction mixture was stirred overnight and then cooled to −10 °C. Filtration yielded 18.5 g (45.2%) of the pure, yellow product (m.p. 43–45 °C). Anal. Found: C, 76.27; H, 6.65. $C_{23}H_{24}NOP$ calcd.: C, 76.43; H, 6.42%.) MS, m/z for M^+: 361, 332, 239, 212, 199, 183, 108. ^{1}H NMR (δ, multiplicity, J): $CH{=}N$ (8.18 ppm, 1, singlet) PPh_2 (7.25, 10, multiplet), C_6H_4 (7.0, 4, multiplet), CH_2N (3.53 ppm, 2, triplet $|^3J(HH)|$ 6 Hz), CH_2CH_2N, CH_2CH_2P and CH_2CH_2P (1.8 ppm, 6, multiplet)}.

$\{Ph_2P(CH_2)_4N{=}CHC_6H_4$-o-O$\}_2Ni$ (VIII). A solution of 0.342 g (1.37 mmol) of $Ni(OAc)_2 \cdot 4H_2O$ and 1.00 g (2.77 mmol) of VII in 50 ml of THF was stirred at ambient temperature under N_2 for 2 days. The solution was then filtered to yield 0.671 g of analytically pure green VIII $\cdot$ $0.5H_2O$. The filtrate was evaporated to dryness, and the oily residue was recrystallized to yield an additional 0.160 g of VIII. Total yield was 76.2%. Anal. Found: C, 70.18; H, 6.16. $C_{46}H_{47}N_2NiO_{2.5}P_2$ calcd.: C, 70.01; H, 5.96%.

$(CO)_5Cr\{Ph_2P(CH_2)_4N{=}CHC_6H_4$-o-OH$\}$ (IX). A solution of 1.86 g (5.15 mmol) of VII and 1.20 g (5.15 mmol) of freshly purified $Cr(CO)_5(CH_3CN)$ in 80 ml of dry hexanes was stirred for 12 h at ambient temperature. The reaction mixture was then filtered, and the filtrate was evaporated to dryness to yield 2.62 g (91.8%) of crude IX. Recrystallization from dichloromethane/hexanes yielded analytically pure, yellow IX (m.p. 93–98 °C). Anal. Found: C, 60.93; H, 4.47; N, 2.39. $C_{28}H_{24}NO_6PC_5$ calcd.: C, 60.76, H, 4.38, N, 2.53%.

trans-$(CO)_4Cr\{Ph_2P(CH_2)_4N{=}CHC_6H_4$-o-OH$\}_2$ (X). A solution of 1.0 g (4.4 mmol) of old $Cr(CO)_5(CH_3CN)$ (stored at room temperature for several weeks) and 1.55 g (4.29 mmol) of VII in 50 ml of degased hexane was stirred under N_2 at ambient temperature for 24 h. The precipitate was collected by filtration and washed with degased hexanes to yield 0.636 g (16.7%) of tan X.

$[(CO)_5Cr\{Ph_2P(CH_2)_4N{=}CHC_6H_4$-o-O$\}]_2Ni$ (XI). A solution of 0.16 g (0.45 mmol) of $Ni(BF_4)_2 \cdot 6H_2O$ and 0.50 g (0.36 mmol) of IX with 0.5 ml of triethylamine in 50 ml of methanol was stirred at ambient temperature under N_2 for 48 h. Evaporation of the mixture to dryness then yielded 0.41 g (78%) of crude XI. Recrystallization from methylene chloride/methanol yielded pure, green XI.

$[(CO)_5Cr\{Ph_2P(CH_2)_4N{=}CHC_6H_4$-o-O$\}]_2Zn$ (XII). A mixture of 0.88 g (1.59

mmol) of IX, 0.20 g (0.88 mmol) of $ZnBr_2$ and 0.30 g (2.2 mmol) of K_2CO_3 in 25 ml of a 1/6 THF/methanol solution was stirred at ambient temperature for 4 days. The solution was then filtered, and the filtrant was taken up in hot dichloromethane. Cooling of the dichloromethane solution yielded 0.59 g (63%) of crude yellow XII.

$(CO)_5W\{Ph_2P(CH_2)_4N{=}CHC_6H_4\text{-}o\text{-}OH\}$ (XIII). A solution of 1.37 g (3.79 mmol) of VII and 1.38 g (3.78 mmol) of freshly purified $W(CO)_5(CH_3CN)$ in 50 ml of dry hexanes was stirred under N_2 at ambient temperature for 12 h. The reaction mixture was then filtered, and the filtrate was evaporated to dryness to yield 2.29 g (88.3%) of crude XIII. Recrystallization from dichloromethane/hexanes yielded analytically pure, yellow XIII (m.p. 95–96 °C). Anal. Found: C, 49.18; H, 3.54; N, 2.04. $C_{28}H_{24}NO_6PW$ calcd.: C, 49.07; H, 3.54; N, 2.04.

$[(CO)_5W\{Ph_2P(CH_2)_4N{=}CHC_6H_4\text{-}o\text{-}O\}]_2Ni$ (XIV). Route 1. A solution of 0.500 g (0.730 mmol) of XIII, 0.125 g (0.365 mmol) of $Ni(BF_4)_2 \cdot 6H_2O$, and 0.20 ml (1.46 mmol) of triethylamine in 40 ml of THF was stirred at room temperature under N_2 for 18 h. The solution was then filtered, and the filtrate was evaporated to dryness to yield 0.521 g (100%) of crude XIV. Recrystallization from dichloromethane/diethyl ether yielded analytically pure, green XIV. Anal. Found: C, 47.16; H, 3.28; 1.89. $C_{56}H_{46}N_2NiO_{12}P_2W_2$ calcd.: C, 47.14; H, 3.22; N, 1.96%.

Route 2. A solution of 0.50 g (0.64 mmol) of VIII and 0.47 g (1.3 mmol) of freshly purified $(CO)_5W(CH_3CN)$ in 50 ml of dry dichloromethane was stirred at ambient temperature for 12 h. The reaction solution was evaporated to dryness to yield 0.78 g (86%) of crude XIV.

$[(CO)_5W\{Ph_2P(CH_2)_4N{=}CHC_6H_4\text{-}o\text{-}O\}]_2Cu$ (XV). A solution of 0.30 g (0.44 mmol) of XIII, 0.12 ml (0.88 mmol) of triethylamine and 0.060 g (0.22 mmol) of $Cu(OAc)_2 \cdot H_2O$ in 50 ml of methanol was stirred at ambient temperature for 24 h. The reaction mixture was then evaporated to dryness. The residue was washed with 20 ml of a 1/1 hexanes/water mixture to yield 0.28 g (89%) of crude XV. Recrystallization from dichloromethane/hexanes yielded analytically pure, green-brown XV. Anal. Found: C, 47.06; H, 3.28; N, 1.94. $C_{56}H_{46}N_2CuO_{12}P_2W_2$ calcd.: C, 46.96; H, 3.24; N, 1.96%.

$[(CO)_5W\{Ph_2P(CH_2)_4N{=}CHC_6H_4\text{-}o\text{-}O\}]_2Zn$ (XVI). A solution of 1.0 ml (1.1 mmol) of a 1.1 M solution of diethylzinc in toluene in 25 ml of dry THF was added dropwise to a solution of 0.50 g (0.73 mmol) of XIII in 50 ml of dry THF. The reaction mixture was stirred for 24 h and then was evaporated to dryness. A ^1H NMR spectrum of the residue indicated that the reaction had not gone to completion. The residue was dissolved in 25 ml of THF, and 1.0 ml of a 1.1 *M* solution of diethylzinc in toluene was added. This solution was stirred for 12 h and then was evaporated to dryness. The residue was dissolved in 25 ml of a 1/1 mixture of methylene chloride and hexanes, and the resulting solution was filtered through a 30 cc medium sintered glass filter. The filtrate was evaporated to dryness and then washed with two, 25 ml portions of hexanes to yield 0.29 g (55%) of pale yellow, crude XVI.

Collection and reduction of X-ray data

Brown needles of $[(CO)_5Mo\{P(OCH_2CMe_2CH_2O)NH(CH_2)_2N{=}CHC_6H_4\text{-}o\text{-}O\}]_2Cu$ (XVII) were grown by diffusion of methanol into a THF solution of the complex. A suitable crystal was mounted in a capillary on an Enraf Nonius CAD-4

Table 4

Crystallographic data for compound XVII

Compound	$CuMo_2C_{38}H_{40}P_2O_{16}N_4$
Mol wt	1126.12
Space group	$P\bar{1}$
Cell constants	
a, Å	6.613(2)
b, Å	9.725(4)
c, Å	18.725(7)
α, deg	93.65(3)
β, deg	99.07(4)
γ, deg	102.85(4)
Cell vol., Å	1153.3
Molecules/unit cell	1
ρ (calcd.), gcm^{-3}	1.62
μ (calcd.), cm^{-1}	11.42
radiation	Mo-K_{α}
Max. crystal dimensions, mm	$0.20 \times 0.15 \times 0.12$
Scan width, deg	$0.80 + 0.20 \tan(\theta)$
Stnd reflections	3 0 0, 0 2 0, 0 0 5
Decay of stnds	less than 0.03
2θ range	2–44°
Reflections measured	3057
Reflections observed	2267
No. of parameters varied	284
GOF	0.83
R	0.043
R_w	0.049

diffractometer. Final unit cell parameters, given in Table 4, were obtained by a least squares fit of the angles of 24 accurately centered reflections ($2\theta > 25°$). Details of the data collection methods have previously been reported [23]. Lorentz, polarization and empirical absorption (ψ scan) corrections were applied to the data.

Solution and refinement of the structure

The cell parameters indicated a choice of either $P1$ or $P\bar{1}$ as the space group. The centric $P\bar{1}$ was chosen to be the correct one on the basis of the successful refinement of the structure. The Cu atom was located by heavy-atom methods with the aid of the SHELX computer program system [24], and the remaining non-hydrogen atoms were located by subsequent difference Fourier syntheses. Refinement of the non-hydrogen atoms with anisotropic thermal parameters and inclusion of the hydrogen atoms at calculated positions converged at $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.043$ and $R_\omega = (\Sigma\omega(|F_o| - |F_c|)^2/\Sigma|F_o|^2)^{0.5} = 0.049$ based on 2267 unique observed reflections. In the last stage of refinement no parameter shifted by more than 0.01 of its standard deviation. Neutral atom scattering factors for non-hydrogen atoms were taken from the compilations of Cromer and Weber [25], and those for hydrogen atoms were taken from "International Tables for X-Ray Crystallography" [26]. Corrections for the real and imaginary components of anomalous dispersion were taken from the compilations of Cromer and Liberman [27] and were applied to the

Table 5

Positional parameters with e.s.d.s for XVII [a]

Atom	x/a	y/b	z/c
Cu	1.0000	0.0000	1.0000
Mo	0.6578(1)	−0.19188(7)	0.61280(4)
P	0.5903(3)	−0.3138(2)	0.7216(1)
N(1)	1.079(1)	−0.1323(7)	0.9279(3)
N(2)	0.760(1)	−0.2486(7)	0.7956(3)
O(1)	1.2082(9)	0.1552(6)	0.9817(3)
O(2)	0.3676(8)	−0.3239(5)	0.7500(3)
O(3)	0.6005(7)	−0.4769(5)	0.7204(3)
O(4)	0.580(1)	0.0927(7)	0.6843(5)
O(5)	0.179(1)	−0.2666(8)	0.5329(4)
O(6)	1.134(1)	−0.0789(7)	0.6915(4)
O(7)	0.760(1)	−0.060(1)	0.4694(5)
O(8)	0.743(1)	−0.4724(8)	0.5414(4)
C(1)	1.366(1)	0.1562(9)	0.9473(5)
C(2)	1.525(2)	0.283(1)	0.9536(5)
C(3)	1.693(1)	0.290(1)	0.9168(6)
C(4)	1.710(2)	0.175(1)	0.8756(7)
C(5)	1.559(2)	0.054(1)	0.8682(6)
C(6)	1.387(1)	0.0400(9)	0.9045(5)
C(7)	1.244(1)	−0.0957(9)	0.8973(5)
C(8)	0.963(1)	−0.2803(9)	0.9124(5)
C(9)	0.749(1)	−0.2972(9)	0.8672(4)
C(10)	0.189(1)	−0.4277(9)	0.7093(5)
C(11)	0.217(1)	−0.5755(9)	0.7102(5)
C(12)	0.417(1)	−0.5795(9)	0.6792(5)
C(13)	0.232(2)	−0.623(1)	0.7857(6)
C(14)	0.033(1)	−0.673(1)	0.6567(6)
C(15)	0.604(1)	−0.010(1)	0.6582(5)
C(16)	0.348(1)	−0.2453(9)	0.5626(5)
C(17)	0.966(1)	−0.1211(9)	0.6624(5)
C(18)	0.726(1)	−0.103(1)	0.5226(6)
C(19)	0.713(1)	−0.372(1)	0.5676(5)

[a] Atoms numbered as shown in Fig. 1.

Mo, Cu and P atoms. The final values of the positional parameters are given in Table 5, and those for the bond lengths and bond angles for non-hydrogen atoms are given in Table 6.

Results and discussion

Synthesis

Two different synthetic methods were used to prepare the heterotrimetallic complexes. The first, shown in eq. 1, involves the reactions of coordinated P-donor ligands and is similar to the route we have reported for the preparations of other heterotrinuclear complexes with bridging phosphinamide-salicylaldiminate ligands

Table 6

Important bond lengths (Å) and angles (°) with e.s.d.s for XVII [a]

Atoms	Distance	Atoms	Distance
Cu-N(1)	2.011(7)	Cu-O(1)	1.893(5)
Mo-P	2.472(2)	Mo-C(15)	2.04(1)
Mo-C(16)	2.052(9)	Mo-C(17)	2.044(9)
Mo-C(18)	2.01(1)	Mo-C(19)	2.03(1)
P-N(2)	1.633(7)	P-O(2)	1.628(5)
P-O(3)	1.601(5)	N(1)-C(7)	1.31(1)
N(1)-C(8)	1.46(1)	N(2)-C(9)	1.46(1)
O(1)-C(1)	1.31(1)	O(2)-C(10)	1.444(9)
O(3)-C(12)	1.458(9)	O(4)-C(15)	1.14(1)
O(5)-C(16)	1.134(9)	O(6)-C(17)	1.131(9)
O(7)-C(18)	1.14(1)	O(8)-C(19)	1.13(1)
C(1)-C(2)	1.42(1)	C(1)-C(6)	1.39(1)
C(2)-C(3)	1.39(1)	C(3)-C(4)	1.35(1)
C(4)-C(5)	1.35(1)	C(5)-C(6)	1.40(1)
C(6)-C(7)	1.43(1)	C(8)-C(9)	1.50(1)
C(10)-C(11)	1.49(1)	C(11)-C(12)	1.54(1)
C(11)-C(13)	1.51(1)	C(11)-C(14)	1.54(1)
Atoms	**Angle**	**Atoms**	**Angle**
N(1)′-Cu-O(1)	88.2(3)	N(1)-Cu-O(1)	91.8(3)
P-Mo-C(15)	91.3(3)	P-Mo-C(16)	94.4(2)
C(15)-Mo-C(16)	88.3(3)	P-Mo-C(17)	88.1(2)
C(15)-Mo-C(17)	87.5(3)	C(16)-Mo-C(17)	175.1(3)
P-Mo-C(18)	175.6(3)	C(15)-Mo-C(18)	92.8(4)
C(16)-Mo-C(18)	87.5(4)	C(17)-Mo-C(18)	90.3(4)
P-Mo-C(19)	88.8(3)	C(15)-Mo-C(19)	179.7(2)
C(16)-Mo-C(19)	92.0(3)	C(17)-Mo-C(19)	92.2(3)
C(18)-Mo-C(19)	87.1(4)	Mo-P-N(2)	114.7(2)
Mo-P-O(2)	120.2(2)	N(2)-P-O(2)	101.6(3)
Mo-P-O(3)	117.8(2)	N(2)-P-O(3)	99.8(3)
O(2)-P-O(3)	99.5(3)	Cu-N(1)-C(7)	122.7(6)
Cu-N(1)-C(8)	121.0(5)	C(7)-N(1)-C(8)	116.0(7)
P-N(2)-C(9)	125.1(5)	Cu-O(1)-C(1)	129.6(6)
P-O(2)-C(10)	116.0(5)	P-O(3)-C(12)	116.2(5)
O(1)-C(1)-C(2)	118.5(9)	O(1)-C(1)-C(6)	124.0(7)
C(2)-C(1)-C(6)	117.5(8)	C(1)-C(2)-C(3)	120(1)
C(2)-C(3)-C(4)	121.0(9)	C(3)-C(4)-C(5)	120(1)
C(4)-C(5)-C(6)	122(1)	C(1)-C(6)-C(5)	119.4(8)
C(1)-C(6)-C(7)	122.9(7)	C(5)-C(6)-C(7)	117.7(9)
N(1)-C(7)-C(6)	127.7(8)	N(1)-C(8)-C(9)	112.4(7)
N(2)-C(9)-C(8)	112.0(7)	O(2)-C(10)-C(11)	113.1(6)
C(10)-C(11)-C(12)	107.2(6)	C(10)-C(11)-C(13)	112.1(8)
C(12)-C(11)-C(13)	110.9(7)	C(10)-C(11)-C(14)	108.4(7)
C(12)-C(11)-C(14)	106.2(8)	C(13)-C(11)-C(14)	111.8(7)
O(3)-C(12)-C(11)	111.6(7)	Mo-C(15)-O(4)	178.1(7)
Mo-C(16)-O(5)	175.5(8)	Mo-C(17)-O(6)	177.7(8)
Mo-C(18)-O(7)	176(1)	Mo-C(19)-O(8)	179.0(9)

[a] Atoms numbered as shown in Fig. 1.

$$\begin{array}{c} (CO)_5Mo(Ph_2PCl) + H_2N(CH_2)_3NH_2 \\ \longrightarrow (CO)_5Mo\{Ph_2PNH(CH_2)_3NH_2\} \\ (I) \\ \Big\downarrow \sigma\text{-salicylaldehyde} \\ (CO)_5Mo\{Ph_2PNH(CH_2)_3N{=}CHC_6H_4OH\} \\ (II) \\ \Big\downarrow M^{2+} \\ [(CO)_5Mo\{Ph_2PNH(CH_2)_3N{=}CHC_6H_4O\}]_2M \\ (III\colon M^{2+} = Ni^{2+}; \\ IV\colon M^{2+} = Cu^{2+}) \end{array} \qquad (1)$$

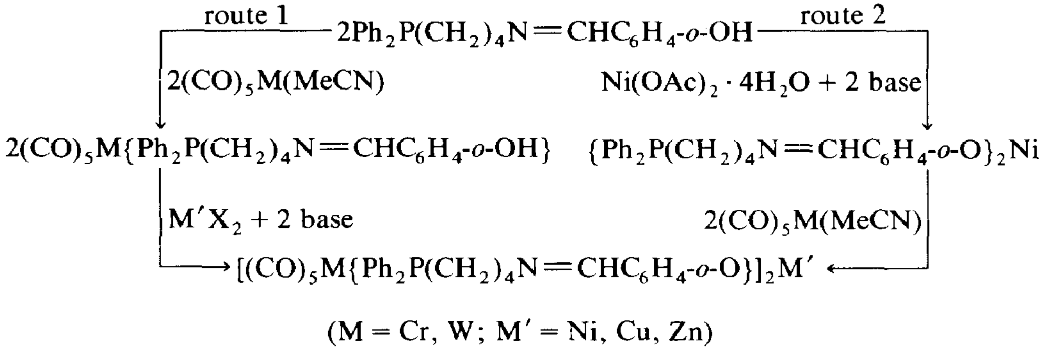
[17,19,20]. This method provides a precise control over the coordination environments of the metals by the sequential synthesis and complexation of the various donor sites of the heteropolydentate ligand. The major limitation of this method is that it is necessary to be able to synthesize stable chlorophosphine complexes of the soft metal with ligands that will not be displaced by the nucleophilic reagents used to synthesize the salicylaldiminate site.

The second method used to prepare the heterotrinuclear complexes involves the sequential reactions of the hard and soft metals with $Ph_2P(CH_2)_4N{=}CHC_6H_4$-*o*-OH (VII). This ligand was chosen because it contains the same number of bridging groups between the P- and *o*-salicylaldiminate-coordination sites as does the $Ph_2PNH(CH_2)_3N{=}CHC_6H_4$-*o*-OH ligand. The only difference in these ligands is the substitution of an amino group by a methylene group.

Ligand VII was synthesized using the procedure of Kraihanazel et al. with minor modifications as shown in eq. 2 [18]. The yield of the pure ligand is low due to its solubility in cold methanol.

$$\begin{tikzcd} Ph_2PH + Bu^nLi \arrow[r, "ether"] & LiPPh_2 \arrow[r, "Br(CH_2)_3CN", "-78^\circ C"'] & Ph_2P(CH_2)_3CN \\ & & (V) \arrow[d, "LiAlH_4"'] \\ Ph_2P(CH_2)_4N{=}CHC_6H_4\text{-}o\text{-}OH & & Ph_2P(CH_2)_4NH_2 \arrow[ll, "\sigma\text{-salicyclaldehyde}"'] \\ (VII) & & (VI) \end{tikzcd} \qquad (2)$$

The heterotrinuclear complexes of VII are prepared by the sequential coordination of the soft and hard metals to the ligands as shown in eq. 3. The order in which the metals are coordinated to VII does not affect the yields of the heterotrinuclear complexes. Route 1 has the advantage that the intermediate mononuclear complexes are air stable and diamagnetic, but has the disadvantage that, as is observed with II, it is difficult to get the reactions of the hard metal dications with the *o*-salicylaldiminate groups to go to completion. This is in contrast to the ease with which the reactions of hard metal dications with complexes of the type $(CO)_5Mo\{R_2PNH(CH_2)_2N{=}CHC_6H_4\text{-}o\text{-}OH\}$ ($R_2 = Ph_2$, $OCH_2CMe_2CH_2O$) [19,20] and with VII go to completion. These results suggest that the conformations of the complexes with a four atom bridge between the P-donor and *o*-salicylaldiminato groups are different from those of the complexes with a three atom bridge between the two groups, and that this affects the abilities of the complexes to coordinate a metal dication. This is discussed in more detail in the spectroscopic and X-ray crystallography sections.



(3)

Spectroscopic studies

The complexes prepared in this project were characterized by IR spectroscopy and multinuclear NMR spectroscopy, if diamagnetic. The ^{13}C NMR spectroscopic data are summarized in Tables 1 and 2, and the ^{31}P NMR and IR spectroscopic data are summarized in Table 3.

The ^{31}P NMR spectroscopic data for the complexes suggest that coordination of a metal dication to the *o*-salicylaldiminato group does not perturb the P environment. Coordination of Ni^{2+} to II causes a downfield shift of 0.30 ppm in the ^{31}P NMR resonance while coordination of Ni^{2+} or Zn^{2+} to IX and XIII causes upfield shifts of 0.06 to 0.25 ppm in their ^{31}P NMR resonances. These small shifts are in contrast to the large shifts in the ^{31}P NMR resonances of the $(CO)_5Mo\{R_2PNH(CH_2)_2N{=}CHC_6H_4\text{-}o\text{-}OH\}$ complexes that are observed upon coordination of Ni^{2+} ($R_2 = Ph_2$, 15.18 ppm upfield; $R_2 = OCH_2CMe_2CH_2O$, 14.30 ppm downfield) [19,20]. The additional bridging atom may prevent the interactions between the P substituents and the *o*-salicylaldiminato groups similar to those observed in complexes with three atom bridges [19,20] from occurring.

The lack of interactions between the two coordination sites in the complexes with four atom bridges is also indicated by the shifts in the ^{13}C NMR resonances of the bridging methylene groups as the P donor and *o*-salicylaldiminato groups are coordinated. Coordination of Ni^{2+} to the *o*-salicylaldiminato groups of II, IX and XIII causes significant shifts in the ^{13}C NMR resonances of the C(3) and C(4) methylenes, but only very small shifts in the ^{13}C NMR resonances of the C(1) and C(2) methylenes. In contrast, coordination of either $(CO)_5Cr$ or $(CO)_5W$ to the diphenylphosphino group of VII causes large shifts in the ^{13}C NMR resonances of the C(1) and C(2) methylenes, but much smaller shifts in the ^{13}C NMR resonances of the C(3) and C(4) methylenes.

The shifts of the imine and phenoxy ^{13}C NMR resonances of the *o*-salicylaldiminato groups in IX and XIII upon coordination of Ni^{2+} or Zn^{2+} are in opposite directions (upfield for Ni^{2+} and downfield for Zn^{2+}) and are significantly larger for Zn^{2+} than for Ni^{2+}. The shifts of the C(3) and C(4) methylene ^{13}C NMR resonances upon coordination of Ni^{2+} or Zn^{2+} to IX and XIII are also quite different. For Ni^{2+}, the ^{13}C NMR resonance of C(3) shifts downfield but that of C(4) shifts upfield. The magnitude of the shift is larger for C(3) than for C(4). In contrast, for Zn^{2+}, the ^{13}C NMR resonance of C(3) shifts upfield while that of C(4) shifts downfield, and the magnitude of the shift is much larger for C(4) than for C(3).

These very different coordination chemical shifts may be due to different coordination geometries of the Ni^{2+} and Zn^{2+} ions in the trinuclear complexes. The fact that III, XI and XIV are all diamagnetic indicates that the Ni^{2+} has a square planar coordination geometry. This is supported by the *d–d* transition at 611 nm (ϵ 48 $cm^{-1}mol^{-1}$) for XI, and by the X-ray crystal structures of similar Ni^{2+} complexes [28]. The spectroscopic data do not provide any information about the coordination environment of the Zn^{2+}. Previous studies of Zn^{2+} complexes with bulky N- and O-donor ligands, suggest that the most likely coordination geometry for Zn^{2+} is tetrahedral [29].

Structure of $[(CO)_5Mo\{P(OCH_2CMe_2CH_2O)NHCH_2CH_2N{=}CHC_6H_4\text{-}o\text{-}O\}]_2Cu$ *(XVII)*

The opposite ^{31}P NMR coordination chemical shifts that are observed when Ni^{2+} is coordinated to complexes of the type $(CO)_5Mo\{R_2P(CH_2)_2N{=}CHC_6H_4\text{-}o\text{-}OH\}$ ($R_2 = Ph_2$, $OCH_2CMe_2CH_2O$) suggest that the solution conformations, and most likely the solid state conformations of these trinuclear complexes are different. The X-ray crystal structures of the complexes $[(CO)_5Mo\{Ph_2PNH(CH_2)_2N{=}CHC_6H_4\text{-}o\text{-}O\}]_2M$ (M = Cu, XVIII, and Ni, XIX) have already been reported [19,20]. Thus, it was of interest to determine the structure of XVII in order to be able to determine the effects of the different P substituents on the solid state conformations of this class of complexes.

The molecular structure of XVII is shown in Fig. 1. Coordinates of the refined atoms are given in Table 5 and pertinent bond lengths and angles are given in Table 6. As is the case for XVIII, the Cu^{2+} ion in XVII occupies an inversion center, and the molecular centrosymmetry necessitates a *trans* square planar arrangement of the *o*-salicylaldiminato ligands about the Cu^{2+}. The lack of tetrahedral distortion in the coordination geometry of the Cu^{2+} is unusual for bis(*o*-salicylaldiminato)copper(II) complexes with bulky N-substituents [30].

The arrangement of ligands about the Mo atoms in XVII is best described as a slightly distorted octahedron, similar to that observed in other $(CO)_5Mo$(P-donor) complexes. The dihedral angles formed by the three equatorial planes of four donor atoms and the molybdenum are 90.3(1), 92.4(1) and 90.1(1). The Mo–C bond for the carbonyl *trans* to the P-donor group is significantly shorter than the average of the Mo–C bonds *cis* to the P-donor group (2.01(1) Å vs. 2.04(1) Å). This is consistent with the P-donor group being a better σ electron donor and a poorer π electron acceptor than is the carbonyl ligand.

The major differences in the structures of XVII and XVIII have to do with the arrangement of the P substituents. A stacking interaction is observed between a phenyl group on each P and the bis(salicylaldiminato)copper(II) group in XVIII. The type of interaction cannot occur in XVII, and the phosphorinane ring is oriented away from the bis(salicylaldiminato)copper(II) group. The overall result is

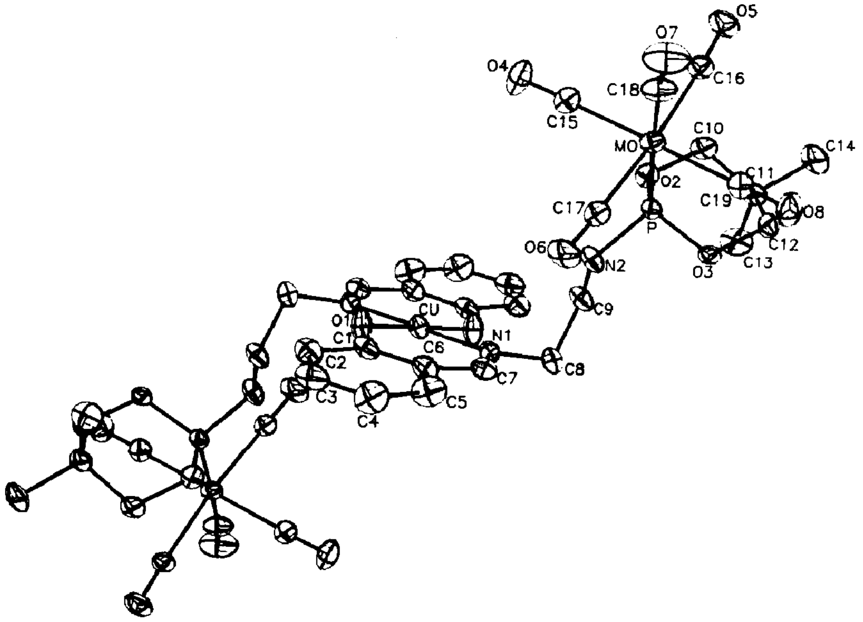


Fig. 1. ORTEP [33] drawing of the molecular structure of *trans*-$[(CO)_5Mo\{P(OCH_2CMe_2CH_2O)NH\text{-}CH_2CH_2N{=}CHC_6H_4\text{-}o\text{-}O\}]_2Cu$ (XVII). Hydrogen atoms are omitted for clarity.

that the conformations of the bridging chains in the two complexes are quite different. The different conformations are reflected in the very different torsion angles for P–N(2)–C(9)–C(8) (148.8° in XVII vs. 135.3° in XVIII) and C(9)–C(8)–N(1)–Cu (−73.5° in XVII vs. −83.9° in XVIII). It seems likely that these different conformations also occur in the solutions structures of these complexes and give rise to the different ^{31}P NMR coordination chemical shifts of the complexes.

Although the conformations of the bridging groups are quite different in XVII and XVIII, the Mo–Cu distances are very similar (7.24 Å in XVII and 7.08 Å (average) in XVIII). This suggests that the metal–metal distance is a function only of the length of the bridging group but that the conformation is a function of both the length of the bridging group and the nature of the P substituents. This may be very useful in the design of heteropolynuclear catalysts for activation of bifunctional organic species because the metal-metal distance and conformation of the complex can be tailored to fit that of the substrate.

A second interesting aspect of the structure of XVII is the conformation of the 1,3,2-dioxaphosphorinane ring. Two crystal structures of molybdenum carbonyl complexes with 1,3,2-dioxaphosphorinane ligands have been reported [31,32]. In these complexes, the 2-substituent was an O, and the larger molybdenum carbonyl group occupied the equatorial position, as expected. In contrast, the 2-substituent in XVII is N, and the molybdenum carbonyl group occupies the axial position. This is surprising because the same synthetic route, the nucleophilic displacement of bromide from $(CO)_5Mo\{P(OCH_2CMe_2CH_2O)Br\}$, was used to prepare XVII and one of the O substituted complexes. This suggests that the mechanism of nucleophilic substitution of bromide from $(CO)_5Mo\{P(OCH_2CMe_2CH_2O)Br\}$ by N and O nucleophiles is quite different.

The ring conformation of the 2,3,2-dioxaphosphorinane is similar to that reported for the earlier complexes. The ring is somewhat flattened about the $P(OC)_2$ group because the P–O–C angles are larger than the tetrahedral angle (average of 116.1(1)°), and the O–P–O angle is smaller than the tetrahedral angle (99.5(3)°). Both of these angles are smaller than those observed in the previously studied complexes, and this may be due to the differences in the conformation about P that were discussed in the previous paragraph.

Conclusions

Unusual heterotrimetallic complexes with bridging P-donor/*o*-salicylaldiminato ligands can be prepared either via the reactions of coordinated P-donor ligands or by the sequential addition of metals to the free ligand. Both the solution and solid state conformations of these ligands are sensitive to the nature of the P substituents, the length of the bridging group between the P and the imine N and to the divalent cation that is coordinated to the *o*-salicylaldiminato ligands. Substitution of a 1,3,2-dioxaphosphorinane for the diphenylphosphino group has a particularly striking effect on the conformation of the complex although it does not affect the metal–metal distance. These results suggest that systematic variation of these parameters should allow the conformations of the complexes to be controlled.

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References

1 F. Senocq, C. Randrianalimanama, A. Thorez, P. Kalck, R. Choukroun and D. Gervais, J. Chem. Soc., Chem. Commun., (1984) 1376.
2 R. Chockroun, D. Gervais, J. Jaud, P. Kalck and F. Senocq, Organometallics, 5 (1986) 67.
3 R. Choukroun, A. Iraqi, D. Gervais, J.-C. Daran and Y. Jeannin, Organometallics, 6 (1987) 1197.
4 R. Choukroun, A. Iraqi, C. Rifai and D. Gervais, J. Organomet. Chem., 353 (1988) 45.
5 G.W. Parshall, Homogeneous Catalysis, Wiley-Interscience, New York, NY, 1980.
6 J. Powell, A. Kuksis, C.J. May, S.C. Nyburg and S.J. Smith, J. Am. Chem. Soc. 103 (1981) 5941.
7 T. Okano, M. Yamomoto, T. Nocuchi, H. Konishi and J. Kiji, Chem. Lett., (1982) 977.
8 J. Powell, S.C. Nyburg and S.J. Smith, Inorg. Chim. Acta, 76 (1983) L75.
9 J. Powell, M. Gregg, A. Kuskis, A. and P. Meindl, J. Am. Chem. Soc., 105 (1983) 1064.
10 B.A. Boyce, A. Carroy, J.-M. Lehn and D.A. Parker, J. Chem. Soc., Chem. Commun., (1984) 1546.
11 T. Okano, Y. Moriyama, H. Konishi and J. Kiji, Chem. Lett., (1986) 1463.
12 T. Okano, M. Iwahara, H. Konishi and J. Kiji, J. Organomet. Chem., 346 (1988) 267.
13 G.E. Lewis and C.S. Kraihanzel, Inorg. Chem., 22 (1983) 2895.
14 D.A. Wrobluski and T.B. Rauchfuss, J. Am. Chem. Soc., 104 (1982) 2314.
15 D.A. Wrobluski, T.B. Rauchfuss, A.L. Rheingold, and K.A. Lewis, Inorg. Chem., 23 (1984) 3124.
16 D.A. Wrobluski, C.S. Day, B.A. Goodman and T.B. Rauchfuss, J. Am. Chem. Soc., 106 (1984) 5464.
17 C.S. Kraihanzel, E. Sinn and G.M. Gray, J. Am. Chem. Soc., 103 (1981) 960.
18 C.S. Kraihanzel and L.A. Wolfe, 16th Middle Atlantic ACS Meeting, April 21–23, 1982.

19 G.M. Gray, A. Zell and H. Einspahr, Inorg. Chem., 25 (1986) 2923.
20 G.M. Gray, N. Takada, A.L. Zell and H.E. Einspahr, J. Organomet. Chem., 342 (1988) 339.
21 C.S. Kraihanzel and C.M. Bartish, J. Organometal. Chem., 43 (1972) 343.
22 U. Koelle, J. Organomet. Chem., 133 (1977) 53.
23 O.T. Beachley, Jr., R.B. Hallock, H. Zhang, and J.L. Atwood, Organometallics, 4 (1985) 1675.
24 G.M. Sheldrick, SHELX76, a system of computer programs for X-ray structural studies, University of Cambridge, Cambridge, UK, 1976.
25 D.T. Cromer and J.T. Weber, Acta Crystallogr., 18 (1965) 104.
26 International Tables for X-ray Crystallography, Vol IV, Kynoch Press, Birmingham, UK, 1974, 72.
27 D.T. Cromer and D.J. Liberman, J. Chem. Phys., 53 (1970) 1891.
28 G.S. Vigee and C.L. Watkins, Inorg. Chim. Acta, 114 (1986) 185.
29 N.N. Greenwood and A. Earnshaw, Chemistry of the Elements, Pergamon Press, Oxford, UK, 1984, p. 1411–1412.
30 V.S. Psalides, P.M. Zorkii and M.A. Porai-Koshits, Vestn. Mosk. Univ. Khim., 16 (1975) 531 and ref..
31 R.A. Jacobsen, B.A. Karcher, R.A. Montag, S.M. Socol, L.J. Van de Griend and J.G. Verkade, Phosphorus and Sulfur, 11 (1981) 27.
32 G.M. Gray and W. Watt, J. Organomet. Chem., 349 (1988) 149.
33 C.F. Johnson, ORTEP: A Fortran Thermal Ellipsoid Program for Crystal Structure Illustrations, Report ORNL-3974, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.