

Synthesis and characterization of a series of *trans*-[Mo(CO)₅(R₂PNHCH₂CH₂N=CHC₆H₄-*o*-O)]₂M (R₂ = Ph₂, OCH₂CMe₂CH₂O; M = Co, Ni, Cu) complexes and the crystal structure of *trans*-[Mo(CO)₅(Ph₂PNHCH₂CH₂N=CHC₆H₄-*o*-O)]₂Ni · 2Et₂O

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Abstract

A series of heterotrinnuclear complexes of the type *trans*-[Mo(CO)₅(R₂PNHCH₂CH₂N=CHC₆H₄-*o*-O)]₂M (R₂ = Ph₂, OCH₂CMe₂CH₂O; M = Co, Ni, Cu) have been synthesized and characterized by multinuclear NMR, IR and VIS-NIR spectroscopy and by measurement of solution magnetic susceptibilities. These studies indicate that the coordination environment of the high spin Co²⁺ ion is octahedral while that of the diamagnetic Ni²⁺ ion is square planar. Coordination of the Ni²⁺ ion to the mononuclear Mo(CO)₅(R₂PNHCH₂CH₂N=CHC₆H₄-*o*-OH) complexes causes quite different effects in the spectra of the diphenylphosphino and dioxaphosphorinane complexes. These differences appear to be due to differences in the intramolecular interactions between the P substituents and bis(salicylaldiminato)M groups.

The molecular structure of *trans*-[Mo(CO)₅(Ph₂PNHCH₂CH₂N=CHC₆H₄-*o*-O)]₂Ni · 2Et₂O has been determined. The complex crystallizes from an HOAc/THF/Et₂O mixture in the monoclinic space group *C*2/*c* (crystal data: *a* 37.71(1), *b* 9.822(1), *c* 17.91(1) Å; α = γ = 90.00(0)°, β 105.45(6)°; *Z* = 4). The Ni²⁺ ion is coordinated to two salicylaldiminato groups in a non-tetrahedrally distorted square planar geometry while the Mo is coordinated to five COs and a P in a slightly distorted octahedral geometry. An interesting feature of the structure is the nearly planar stacking of a phenyl ring on each P with the bis(salicylaldiminato)Ni group.

* G.M.G., N.T. and H.E. mourn the untimely death of a dearly valued colleague, Alan L. Zell.

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Introduction

Transition metal complexes that incorporate more than one reactive, proximal metal site may exhibit catalytic reactivity patterns quite different from those of monometallic catalysts [1]. A number of different polydentate ligand systems have been developed that are capable of forming stable complexes with two or more different transition metal centers. Many of these contain both a phosphine group capable of coordinating to a soft metal center, and one or more donor groups capable of coordinating to a hard metal center. A variety of heteropolynuclear transition metal complexes with P/C-donor bridging ligands such as phosphorus-alkyl ligands [2–4] and phosphorus cyclopentadienyl ligands [5–9] have been synthesized. One of these, a binuclear Rh–Zr exhibits significantly greater activity as a hydroformylation catalyst than does a similar mononuclear Rh complex [2,3]. Complexes with P/N-donor ligands, such as phosphine-amine [10], phosphine-amido [11] and phosphine-*N* heterocyclic ligands [12–15], and with P/O- or P/S-donor ligands, such as phosphinite-crown ether [16–18], phosphine-alkoxide [19] and -thioalkoxide [20], phosphine-carboxylate [21], phosphine-diketonato [22–24] and phosphito ligands [25,26] have also been reported. Ligands with P/N/O-donor sites, such as phosphine- and phosphinite-crown aminoether ligands [16–18,27] and phosphine-salicylaldiminato ligands [28,29] have also been used to form heteropolynuclear complexes.

A common feature of nearly all of the polyheteronuclear complexes described above is the coordination of the metals to two or more bridging ligands, which hold the metal centers in a constrained arrangement. We have undertaken a series of synthetic, spectroscopic and crystallographic studies of polymetallic complexes in which the two metal centers are bridged by a single, multidentate ligand. A preliminary report on the synthesis and X-ray crystal structure of one of these complexes, *trans*-[(CO)₅Mo(Ph₂PNHCH₂CH₂N=CHC₆H₄-*o*-O)]₂Cu · 2THF, has recently been published [29]. In the present paper, the syntheses, multinuclear NMR, IR and VIS-NIR spectroscopic data and magnetic susceptibilities of a series of *trans*-[(CO)₅Mo(R₂PNHCH₂CH₂N=CHC₆H₄-*o*-O)]₂M (R₂ = Ph₂, OCH₂CMe₂-CH₂O; M²⁺ = Co²⁺, Ni²⁺, Cu²⁺) complexes are presented. The molecular structure of *trans*-[(CO)₅Mo(Ph₂PNHCH₂CH₂N=CHC₆H₄-*o*-O)]₂Ni · 2Et₂O is also presented, and the similarities between this structure and that of the *trans*-[(CO)₅Mo(Ph₂PNHCH₂CH₂N=CHC₆H₄-*o*-O)]₂Cu · 2THF complex are discussed.

Experimental

Diethyl ether and THF were distilled from CaH₂ prior to use while other solvents were used as received. Chlorodiphenylphosphine and ethylenediamine were used as received and were stored and transferred under an inert atmosphere. (Chlorodiphenylphosphine)pentacarbonylmolybdenum(0) (I) [30] and (2-bromo-5,5-dimethyl-1,3,2-dioxaphosphorinane)pentacarbonylmolybdenum(0) (II) [31] were prepared by literature methods. All of the complexes were handled under an inert atmosphere when in solution.

Multinuclear NMR spectra of 0.10 *M* chloroform-*d*₁ solutions of all diamagnetic complexes were run on a Nicolet 300 MHz multinuclear NMR spectrometer. The magnetic moments of the paramagnetic complexes were also determined on this

Table 1

¹³C NMR spectroscopic data (0.10 *M* CDCl₃ solutions; δ (ppm), $|^2J(\text{PC})|$ (Hz) in parentheses)

Complex	$\delta(\text{trans-CO})$	$\delta(\text{cis-CO})$	$\delta(\text{P-N-C})$	$\delta(\text{C-C-N})$	$\delta(\text{C=N})$	$\delta(\text{C-O})$
III	210.38d (23.2)	205.60d (9.7)	46.27d (7.8)	42.66d (6.0) ^b		
IV	208.88d (35.4)	205.10d (12.2)	42.87s (<1.0)	42.90d (2.2) ^b		
V	210.15d (22.6)	205.54d (9.7)	44.24d (7.5)	60.69d (5.1) ^b	160.90d	166.82d
VI	208.68d (35.2)	204.92d (13.5)	40.90s (<1.0)	61.09d (4.5) ^b	160.94d	166.84d
VIII	210.18d (23.5)	205.84d (9.8)	45.61d (8.5)	56.80d (4.4) ^b	161.54d	164.71d
XI	208.64d (35.1)	205.01d (12.8)	42.56bs	58.24bs	161.47bs	166.00bs

^as = singlet, d = doublet, b = broad. ^b $|^3J(\text{PC})|$ (Hz).

instrument using the Evan's method [32]. Infrared spectra in the 2100–1800 cm⁻¹ region were run of dilute dichloromethane solutions of the complexes in matched 0.2 mm KBr solution cells on a Perkin–Elmer 283B infrared spectrometer. Full range IR spectra (4000–350 cm⁻¹) were run on KBr pellets of the complexes. Visible-near infrared spectra of 2.0×10^{-2} *M* dichloromethane solutions of the complexes were run on a Cary 14 spectrometer. Mass spectra were run on a Hewlett Packard 5985 GC-MS using an unheated, direct insertion probe. Spectroscopic and magnetic data are summarized in Tables 1 and 2.

Mo(CO)₅(Ph₂PNHCH₂CH₂NH₂) (III)

A solution of 10.0 g (21.91 mmol) of Mo(CO)₅(Ph₂PCl) (I) in 30 ml of THF was added dropwise to a stirred solution of 5.86 ml of ethylenediamine in 10 ml of THF over a 10 min period. This mixture was stirred at ambient temperature for 30 min before being evaporated to dryness. The residue was treated with 100 ml of 1/1 diethyl ether/hexanes, and this mixture was extracted with two, 100 ml portions of water. After drying over MgSO₄, the solution was filtered and the filtrate was reduced in volume to 50 ml by heating under a stream of Ar. Cooling at –10 °C

Table 2

³¹P NMR, IR and VIS-NIR and μ_{eff} data

Complex	$\delta(^{31}\text{P})$ ^a (ppm)	$\nu(\text{CO})$ ^{b,c} (cm ⁻¹)				$\nu(\text{CN})$ ^d (cm ⁻¹)	$\lambda(d-d)$ (ϵ ^e) (nm (cm ⁻¹ <i>M</i> ⁻¹))	μ_{eff} ^f (BM)
		A ₁ ¹	A ₁ ²	B ₁	B ₂			
III	76.98	2073m	1945s	1986w	1932sh			
IV	142.31	2078m	1954s	1993w	1943s			
V	78.54	2078m	1949s	1991w	1932sh	1627m		
VI	142.54	2079m	1951s	1990w	1941sh	1633m		
VII		2075m	1948s	1992w	1935sh	1618m	701(17)	1.87
VIII	63.36	2076m	1948s	1994w	1935sh	1612m	622(57)	
IX		2076m	1949s	1996w	1936sh	1614m	1300(16) 860(5) 578(81)	4.31
X		2078m	1949s	1991w	1940sh	1622m	680(10)	1.72
XI	156.84	2078m	1950s	1993w	1938sh	1612m	617(62)	

^a 0.10 *M* CDCl₃ solution. ^b m = medium, s = strong, sh = shoulder. ^c Dilute CH₂Cl₂. ^d KBr disk. ^e 0.01 *M* CH₂Cl₂. ^f Dilute C₆H₆/CDCl₃.

precipitated the pale-yellow crystalline product. Filtration yielded 7.86 g (74.8%) of $\text{Mo(CO)}_5(\text{Ph}_2\text{PNHCH}_2\text{CH}_2\text{NH}_2)$ (III). Mass spectrum (m/e for ^{98}Mo): 454, 426, 370, 342, 294.

$\text{Mo(CO)}_5(\text{P(OCH}_2\text{CMe}_2\text{CH}_2\text{O)NHCH}_2\text{CH}_2\text{NH}_2)$ (IV)

A solution of 15.72 g (35.0 mmol) of $\text{Mo(CO)}_5(\text{P(OCH}_2\text{CMe}_2\text{CH}_2\text{O)Br})$ (II) and 25.0 ml of ethylenediamine in 50 ml of dry THF was stirred at ambient temperature under Ar for 18 h. The THF was then evaporated to dryness and the residue treated with 200 ml of deionized water. This mixture was stirred at ambient temperature and then filtered to yield 13.56 g (90.5%) of $\text{Mo(CO)}_5(\text{P(OCH}_2\text{CMe}_2\text{CH}_2\text{O)NHCH}_2\text{CH}_2\text{NH}_2)$ (IV). Recrystallization of the complex from dichloromethane/hexanes yielded pure product. Anal. Found: C, 33.55; H, 3.98. $\text{C}_{12}\text{H}_{17}\text{MoN}_2\text{O}_7\text{P}$ calc: C, 33.49; H, 3.95%.

$\text{Mo(CO)}_5(\text{Ph}_2\text{PNHCH}_2\text{CH}_2\text{N=CHC}_6\text{H}_4\text{-o-OH})$ (V)

A solution of 7.17 g (14.9 mmol) of $\text{Mo(CO)}_5(\text{Ph}_2\text{PNHCH}_2\text{CH}_2\text{NH}_2)$ (III) and 1.60 ml of *o*-salicylaldehyde in 50 ml of methanol was stirred under Ar for 4 h. Then the solution was reduced in volume to 30 ml by heating under a stream of Ar before being cooled at -10°C for several hours. Filtration yielded 6.58 g of bright yellow $\text{Mo(CO)}_5(\text{Ph}_2\text{PNHCH}_2\text{CH}_2\text{N=CHC}_6\text{H}_4\text{-o-OH})$ (V). The filtrate was reduced in volume to 10 ml, cooled to -10°C and then filtered to yield an additional 0.53 g of product. The reaction yield was 7.11 g (82.0%). Anal. Found: C, 53.10; H, 3.72. $\text{C}_{26}\text{H}_{20}\text{MoN}_2\text{O}_6\text{P}$ calc: C, 53.42; H, 3.60%.

$\text{Mo(CO)}_5(\text{P(OCH}_2\text{CMe}_2\text{CH}_2\text{O)NHCH}_2\text{CH}_2\text{N=CHC}_6\text{H}_4\text{-o-OH})$ (VI)

A solution of 5.00 g (11.7 mmol) of $\text{Mo(CO)}_5(\text{P(OCH}_2\text{CMe}_2\text{CH}_2\text{O)NHCH}_2\text{CH}_2\text{NH}_2)$ (IV) and 1.25 ml (11.7 mmol) of *o*-salicylaldehyde in 50 ml of methanol was stirred at ambient temperature for 18 h under Ar. The yellow insoluble product was then filtered from the solution and recrystallized from diethyl ether/hexanes to yield 3.93 g (63.1%) of pure $\text{Mo(CO)}_5(\text{P(OCH}_2\text{CMe}_2\text{CH}_2\text{O)NHCH}_2\text{CH}_2\text{N=CHC}_6\text{H}_4\text{-o-OH})$ (VI). Anal. Found: C, 42.83, H, 3.94. $\text{C}_{19}\text{H}_{20}\text{MoN}_2\text{O}_8$ calc: C, 42.70; H, 3.93%.

$[\text{Mo(CO)}_5(\text{Ph}_2\text{PNHCH}_2\text{CH}_2\text{N=CHC}_6\text{H}_4\text{-o-O})]_2\text{Cu} \cdot 2\text{THF}$ (VII $\cdot$ 2THF)

A mixture of 0.341 g (1.71 mmol) of $\text{Cu(OAc)}_2 \cdot \text{H}_2\text{O}$ and 2.00 g (3.42 mmol) of $\text{Mo(CO)}_5(\text{Ph}_2\text{PNHCH}_2\text{CH}_2\text{N=CHC}_6\text{H}_4\text{-o-OH})$ (V) in 25 ml of THF was stirred under Ar at ambient temperature for 42 h. This mixture, which changed from a bright yellow to dark green overnight, was then filtered, and the filtrate was evaporated to dryness to yield 2.35 g (100%) of dark green $[\text{Mo(CO)}_5(\text{Ph}_2\text{PNHCH}_2\text{CH}_2\text{N=CHC}_6\text{H}_4\text{-o-O})]_2\text{Cu}$ (VII). Recrystallization of the complex from THF/diethyl ether yielded pure $[\text{Mo(CO)}_5(\text{Ph}_2\text{PNHCH}_2\text{CH}_2\text{N=CHC}_6\text{H}_4\text{-o-O})]_2\text{Cu} \cdot 2\text{THF}$, (VII $\cdot$ 2THF). Anal. Found: C, 52.23; H, 4.09. $\text{C}_{62}\text{H}_{56}\text{CuMo}_2\text{N}_2\text{O}_{14}$ calc: C, 52.43; H, 4.11%.

$[\text{Mo(CO)}_5(\text{Ph}_2\text{PNHCH}_2\text{CH}_2\text{N=CHC}_6\text{H}_4\text{-o-O})]_2\text{Ni} \cdot 0.5\text{Et}_2\text{O}$ (VIII $\cdot$ 0.5Et₂O)

Using the procedure described for the synthesis of $[\text{Mo(CO)}_5(\text{Ph}_2\text{PNHCH}_2\text{CH}_2\text{N=CHC}_6\text{H}_4\text{-o-O})]_2\text{Cu}$ (VII), 1.00 g (1.71 mmol) of $\text{Mo(CO)}_5(\text{Ph}_2\text{PNHCH}_2\text{CH}_2\text{N=CHC}_6\text{H}_4\text{-o-OH})$ (V) and 0.213 g (0.855 mmol) of $\text{Ni(OAc)}_2 \cdot 4\text{H}_2\text{O}$ yielded 1.25 g

(100%) of crude $[\text{Mo}(\text{CO})_5(\text{Ph}_2\text{PNHCH}_2\text{CH}_2\text{N}=\text{CHC}_6\text{H}_4\text{-}o\text{-O})]_2\text{Ni}$ (VIII). Recrystallization of the complex from dichloromethane/diethyl ether yielded pure $[\text{Mo}(\text{CO})_5(\text{Ph}_2\text{PNHCH}_2\text{CH}_2\text{N}=\text{CHC}_6\text{H}_4\text{-}o\text{-O})]_2\text{Ni} \cdot 0.5\text{Et}_2\text{O}$, (VIII $\cdot 0.5\text{Et}_2\text{O}$). Anal. Found: C, 51.22; H, 4.06 for $\text{C}_{56}\text{H}_{45}\text{Mo}_2\text{N}_2\text{NiO}_{12.5}$ calc: C, 51.37; H, 3.59%.

$[\text{Mo}(\text{CO})_5(\text{Ph}_2\text{PNHCH}_2\text{CH}_2\text{N}=\text{CHC}_6\text{H}_4\text{-}o\text{-O})]_2\text{Co} \cdot 2\text{H}_2\text{O}$ (IX $\cdot 2\text{H}_2\text{O}$)

Using the procedure described for the synthesis of $[\text{Mo}(\text{CO})_5(\text{Ph}_2\text{PNHCH}_2\text{CH}_2\text{N}=\text{CHC}_6\text{H}_4\text{-}o\text{-O})]_2\text{Cu}$ (VII), 2.00 g (3.42 mmol) of $\text{Mo}(\text{CO})_5(\text{Ph}_2\text{PNHCH}_2\text{CH}_2\text{N}=\text{CHC}_6\text{H}_4\text{-}o\text{-OH})$ (V) and 0.427 g (1.71 mmol) of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ yielded 2.06 g (95.5%) of crude $[\text{Mo}(\text{CO})_5(\text{Ph}_2\text{PNHCH}_2\text{CH}_2\text{N}=\text{CHC}_6\text{H}_4\text{-}o\text{-O})]_2\text{Co}$ (IX). The complex was triturated with 1/1 diethyl ether/hexanes for several days to yield pure $[\text{Mo}(\text{CO})_5(\text{Ph}_2\text{PNHCH}_2\text{CH}_2\text{N}=\text{CHC}_6\text{H}_4\text{-}o\text{-O})]_2\text{Co} \cdot 2\text{H}_2\text{O}$ (IX $\cdot 2\text{H}_2\text{O}$) as a brown, powdery solid. Anal. Found: C, 49.01; H, 3.40. $\text{C}_{54}\text{H}_{44}\text{CoMo}_2\text{N}_2\text{O}_{14}$ calc: C, 49.50; H, 3.51%.

$[\text{Mo}(\text{CO})_5(\text{P}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\text{NHCH}_2\text{CH}_2\text{N}=\text{CHC}_6\text{H}_4\text{-}o\text{-O})]_2\text{Cu}$ (X)

Using the procedure described for the synthesis of $[\text{Mo}(\text{CO})_5(\text{Ph}_2\text{PNHCH}_2\text{CH}_2\text{N}=\text{CHC}_6\text{H}_4\text{-}o\text{-O})]_2\text{Cu}$ (VII), 1.06 g (2.00 mmol) of $\text{Mo}(\text{CO})_5(\text{P}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\text{NHCH}_2\text{CH}_2\text{N}=\text{CHC}_6\text{H}_4\text{-}o\text{-OH})$ (VI) and 0.200 g (1.00 mmol) of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ yielded 1.09 g (97.3%) of $[\text{Mo}(\text{CO})_5(\text{P}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\text{NHCH}_2\text{CH}_2\text{N}=\text{CHC}_6\text{H}_4\text{-}o\text{-O})]_2\text{Cu}$ (X). Recrystallization of the complex from dichloromethane/hexanes yielded pure $[\text{Mo}(\text{CO})_5(\text{P}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\text{NHCH}_2\text{CH}_2\text{N}=\text{CHC}_6\text{H}_4\text{-}o\text{-O})]_2\text{Cu}$ (X). Anal. Found: C, 40.62; H, 3.62; N, 4.97. $\text{C}_{38}\text{H}_{38}\text{CuMo}_2\text{N}_4\text{O}_{16}\text{P}_2$ calc: C, 40.53; H, 3.58; N, 4.98%.

$[\text{Mo}(\text{CO})_5(\text{P}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\text{NHCH}_2\text{CH}_2\text{N}=\text{CHC}_6\text{H}_4\text{-}o\text{-O})]_2\text{Ni}$ (XI)

Using the procedure described for the synthesis of $[\text{Mo}(\text{CO})_5(\text{Ph}_2\text{PNHCH}_2\text{CH}_2\text{N}=\text{CHC}_6\text{H}_4\text{-}o\text{-O})]_2\text{Cu}$ (VII), 1.06 g (2.00 mmol) of $\text{Mo}(\text{CO})_5(\text{P}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\text{NHCH}_2\text{CH}_2\text{N}=\text{CHC}_6\text{H}_4\text{-}o\text{-OH})$ (VI) and 0.249 g (1.00 mmol) of $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ yielded 1.03 g (91.9%) of $[\text{Mo}(\text{CO})_5(\text{P}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\text{NHCH}_2\text{CH}_2\text{N}=\text{CHC}_6\text{H}_4\text{-}o\text{-O})]_2\text{Ni}$ (XI). Recrystallization of the complex from dichloromethane/hexanes yielded pure material. Anal. Found: C, 40.62; H, 3.62; N, 4.96. $\text{C}_{38}\text{H}_{38}\text{Mo}_2\text{N}_4\text{NiO}_{16}\text{P}_2$ calc: C, 40.70; H, 3.60; N, 5.00%.

Collection and reduction of X-ray data

Green needles of VIII $\cdot 2\text{Et}_2\text{O}$ were grown by slow cooling of a 1/4 THF/diethyl ether mixture, to which 5 drops of glacial acetic acid had been added. A suitable crystal was mounted on a glass fiber with epoxy cement. The space group and unit cell parameters were determined by use of precession and Weissenberg X-ray photographs. Data collection was carried out using a Picker FACS-1 four-circle diffractometer with Ni-filtered, Cu-K_α (λ 1.5418 Å) radiation. Least-squares analyses of 12 medium resolution reflections gave orientation matrices for the calculation of the setting angles and the final cell parameters. Three reflections were remeasured periodically during data collection to monitor for crystal decay. Decay of approximately 15% was observed during the data collection, and a linear decay correction was applied. The data were processed using the Enraf–Nonius SDP series of programs. Variances were assigned to I s on the basis of counting statistics, with the addition of an instrumental uncertainty term, $(0.03S)^2$, S being the scan count.

Lorentz, polarization and analytical absorption corrections were made to I_s and $\sigma^2 s$.

Solution and refinement of the structure

Compound VIII · 2Et₂O crystallizes in the space group $C2/c$, with the Ni²⁺ ions located on centers of symmetry so that one half molecule constitutes the asymmetric unit. The positions of the Mo, Ni and P atoms were obtained from the Patterson function, and the remainder of the non-H atoms were located by Fourier methods. The structure was refined by a full-matrix least-squares procedure that minimized $w(|F_o| - 1/k|F_c|)^2$, where $w = 1/\sigma^2(F_o)$. Final cycles of refinement varied k , positional and anisotropic thermal parameters for the non-H atoms, positional and isotropic thermal parameters for non-ether H atoms (located in a difference Fourier), and a secondary extinction parameter. Since one half of the ether of crystallization was found to be disordered, the final model included two sites for one of the methylene carbons with fixed occupancies of 0.65 and 0.35. Two sets of coordinates for the methylene and methyl hydrogen atoms in this half of the molecule with fixed

Table 3
Crystallographic data and data collection procedures

Formula	Mo ₂ NiP ₂ O ₁₄ N ₄ C ₆₀ H ₆₀
Molecular weight	1373.69
Crystal system	monoclinic
Space group	$C2/c$
a (Å)	37.71(2)
b (Å)	9.822(3)
c (Å)	17.91(1)
α (°)	90.000(0)
β (°)	105.45(6)
γ (°)	90.000(0)
V (Å ³)	6392.8(10.7)
Z	4
d_{calc} (g/cm ³)	1.273
Crystal size (mm)	0.42 × 0.15 × 0.07
Absorption coefficient (cm ⁻¹)	45.693
Radiation (Å)	Cu- K_{α} , 1.5418
Temperature (°)	21
Collection range	2θ of 2.0–128° (+ h , + k , ± l)
Aperture width (mm)	3
Maximum counting time (s)	72
Scan speed (°/min)	2.0
Scan range (°)	1.8 + 0.285tan θ
Background time (s)	10
Number of unique data	5135
Number of data with $I \geq 0$	5097
Number of variables	486
R (%)	4.1
R_w (%)	4.4
e.s.d.	1.611
Extinction coefficient	3.17298×10^{-7}

coordinates, occupancies and thermal parameters were also included in the final model. Atomic scattering factors were from the Tables of Cromer and Waber [33]. At convergence (max. shift/esd = 0.06 for the non-ether atoms), the R value ($\sum ||F_o| - 1/k|F_c|| / \sum |F_o|$) is 0.041 and the goodness-of-fit ($[\sum w(|F_o| - 1/k|F_c|)^2 / \nu]^{0.5}$, where ν = the number of observations minus the number of variables) is 1.19, considering all 5135 data. Extrema in the final difference Fourier map did not exceed $0.55 \text{ e } \text{\AA}^3$ in magnitude. Relevant crystal and experimental data for compound VIII $\cdot 2\text{Et}_2\text{O}$ are listed in Table 3. Tables of calculated atomic coordinates, thermal parameters, non-essential bond lengths and angles, least squares planes, closest intermolecular contacts and structure factors, and drawings of the unit cell and Et_2O molecule are available from the authors.

Results and discussion

Syntheses

All of the heterobimetallic complexes in this study were prepared by the sequence of reactions outlined in Fig. 1. This scheme is similar to that previously used for the synthesis of *trans*-[*cis*- $\text{Mo}(\text{CO})_4(\text{Ph}_2\text{PNHCH}_2\text{CH}_2\text{N}=\text{CHC}_6\text{H}_4\text{-}o\text{-}\text{O})_2$] Ni (XII) [28]. This method provides a precise control over the coordination environment of the metals by the sequential synthesis and complexation of the various donor sites of the heteropolydentate ligand. The initial coordination of Ph_2Cl to the $(\text{CO})_5\text{Mo}$ group greatly simplifies the handling of the various intermediates since, unlike free

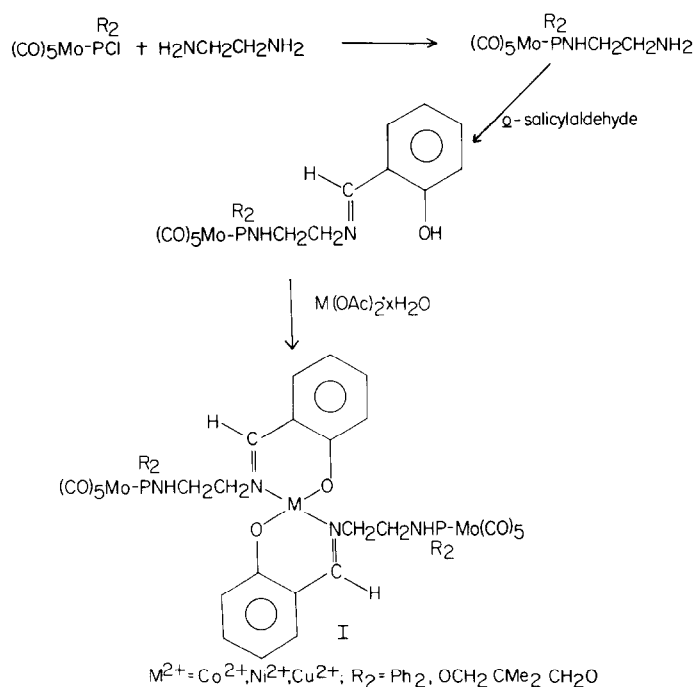


Fig. 1. Synthetic scheme for the *trans*-[$\text{Mo}(\text{CO})_5(\text{R}_2\text{PNHCH}_2\text{CH}_2\text{N}=\text{CHC}_6\text{H}_4\text{-}o\text{-}\text{O})_2$] M ($\text{R}_2 = \text{Ph}_2, \text{OCH}_2\text{CMe}_2\text{CH}_2\text{O}$; $\text{M} = \text{Co}, \text{Ni}, \text{Cu}$) complexes.

P-donor ligands, they cannot undergo Arbuzov rearrangements, are dioxygen and water stable and are easily purified by crystallization. Finally, and perhaps most importantly, this method may be used to synthesize a variety of heteropolynuclear complexes by varying the chlorophosphine complex used, by replacing the *o*-salicylaldimino group with similar groups such as a β -ketoimino group and by varying the metal cation which is coordinated to this group in the last step.

Characterization of the complexes

All complexes were characterized by IR and VIS-NIR spectroscopy, by measurement of solution magnetic susceptibilities and by ^{13}C and ^{31}P NMR spectroscopy, if diamagnetic, and the results are reported in Tables 1 and 2. The CO IR stretching frequencies and ^{13}C NMR chemical shifts and P–C NMR coupling constants of the CO ligands of complexes III–XI are similar to those observed for other $\text{Mo}(\text{CO})_5$ complexes with aminodiphenylphosphine and 2-amino-5,5-dimethyl-1,3,2-dioxaphosphorinane ligands [31,34,35]. The lack of variation in the ^{13}C NMR chemical shifts and the IR stretching frequencies of the CO ligands suggests that coordination of a M^{2+} ion to the salicylaldiminato group has little effect upon the $\text{Mo}(\text{CO})_5$ group.

Coordination of the M^{2+} ion does have significant effects upon the IR absorptions and ^{13}C and ^{31}P NMR chemical shifts of groups closer to the coordination site. The frequencies of the C=N IR absorptions of V and VI are reduced by 5–21 cm^{-1} upon coordination. The ^{13}C NMR resonances of the methylene and salicylaldiminato groups of V and VI also shift upon coordination of Ni^{2+} , and the shifts are of approximately the same magnitudes and in the same directions for the two complexes. In contrast, the coordination of Ni^{2+} to V and VI has significantly different effects upon the ^{31}P chemical shifts of the two complexes. The ^{31}P NMR resonance of VI is shifted 15 ppm upfield upon coordination while that of VI is shifted 15 ppm downfield. The large shifts are most likely due to changes in the conformation at the P since the sensitivity of the ^{31}P NMR resonance to conforma-

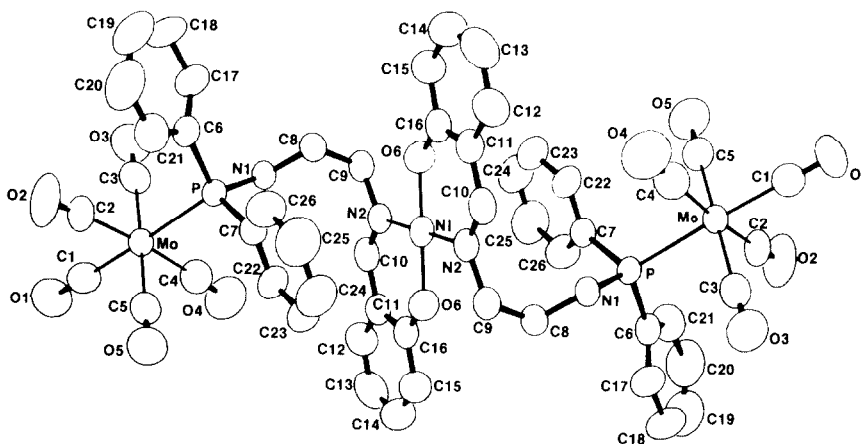


Fig. 2. ORTEP [42] drawing of the molecular structure of *trans*- $[\text{Mo}(\text{CO})_5(\text{Ph}_2\text{PNHCH}_2\text{CH}_2\text{N}=\text{CHC}_6\text{H}_4\text{-}o\text{-O})]_2\text{Ni}$ (VIII). Atoms represented by thermal ellipsoids are drawn at the 25% level. The H atoms have been omitted for clarity.

tional changes is well documented [36], and the NMR and IR data of the $\text{Mo}(\text{CO})_5$ groups exhibit little variation upon coordination of the Ni^{2+} group. The difference in the direction of the shifts in the resonances indicates that the conformational changes which occur upon coordination of the Ni^{2+} in the two complexes are quite different.

The VIS-NIR spectra and solution magnetic susceptibilities of the trimetallic complexes provide insight into the coordination geometries of the M^{2+} ion. Both VIII and XI are diamagnetic in solution and the wavelengths of their single UV-VIS absorptions indicate that the Ni^{2+} ion is in a square planar coordination environment [37]. The solution magnetic susceptibility of IX indicates that the complex

Table 4

Positional parameters with e.s.d.'s for VIII·2Et₂O^a

Atom	x	y	z	Atom	x	y	z
Mo	0.17171(1)	0.22946(3)	-0.04663(1)	Ni	0.0000(0)	0.0000(0)	0.0000(0)
P	0.13685(2)	0.06253(8)	0.01361(4)	O(1)	0.2178(1)	0.4374(3)	-0.1160(2)
O(2)	0.2314(1)	0.0088(3)	-0.0562(2)	O(3)	0.2150(1)	0.3144(4)	0.1250(2)
O(4)	0.1082(1)	0.4458(3)	-0.0639(2)	O(5)	0.1315(1)	0.1365(4)	-0.2163(2)
O(6)	-0.0223(1)	0.0906(2)	-0.0894(1)	O(1E)	0.1362(1)	0.3669(3)	0.1944(2)
N(1)	0.1151(1)	0.1359(2)	0.0724(1)	N(2)	0.0311(1)	0.1527(3)	0.0423(1)
C(1)	0.2008(1)	0.3641(4)	-0.0900(2)	C(2)	0.2102(1)	0.0874(4)	-0.0503(2)
C(3)	0.1995(1)	0.2860(4)	0.0647(2)	C(4)	0.1313(1)	0.3688(4)	-0.0548(2)
C(5)	0.1455(1)	0.1695(4)	-0.1552(2)	C(6)	0.1672(1)	-0.0688(3)	0.0683(2)
C(7)	0.0996(1)	-0.0318(3)	-0.0519(2)	C(8)	0.0923(1)	0.0625(3)	0.1133(2)
C(9)	0.0586(1)	0.1425(2)	0.1178(2)	C(10)	0.0296(1)	0.2683(3)	0.0086(2)
C(11)	0.0062(1)	0.3079(3)	-0.0645(2)	C(12)	0.0078(1)	0.4423(4)	-0.0910(2)
C(13)	-0.0139(1)	0.4834(4)	-0.1610(2)	C(14)	-0.0382(1)	0.3925(5)	-0.2065(2)
C(15)	-0.0406(1)	0.2617(4)	-0.1827(2)	C(16)	-0.0189(1)	0.2148(4)	-0.1102(2)
C(17)	0.1800(1)	-0.0598(4)	0.1477(2)	C(18)	0.2058(1)	-0.1517(6)	0.1893(3)
C(19)	0.2190(1)	-0.2499(5)	0.1538(3)	C(20)	0.2074(1)	-0.2616(4)	0.0757(4)
C(21)	0.1815(1)	-0.1713(4)	0.0309(2)	C(22)	0.0743(1)	0.0411(4)	-0.1078(2)
C(23)	0.0450(1)	-0.0220(4)	-0.1582(2)	C(24)	0.0408(1)	-0.1585(5)	-0.1549(3)
C(25)	0.0645(1)	-0.2318(4)	-0.1009(3)	C(26)	0.0943(1)	-0.1705(4)	-0.0493(2)
C(1E)	0.1382(2)	0.5067(6)	0.2003(3)	C(2E)	0.1204(2)	0.5679(6)	0.1271(3)
C(3E)	0.1406(3)	0.3128(11)	0.2809(7)	C(3E')	0.1697(4)	0.3143(20)	0.2538(8)
C(4E)	0.1652(4)	0.2530(9)	0.3015(5)				
HN(1)	0.1227(7)	0.213(3)	0.092(2)	HC(8A)	0.1049(7)	0.040(3)	0.164(1)
HC(8B)	0.0858(7)	-0.023(3)	0.085(2)	HC(9A)	0.0644(7)	0.232(3)	0.135(2)
HC(9B)	0.0472(7)	0.097(3)	0.152(2)	HC(10)	0.0432(6)	0.333(3)	0.033(1)
HC(12)	0.0232(8)	0.498(3)	-0.063(2)	HC(13)	-0.0130(9)	0.571(3)	-0.176(2)
HC(14)	-0.0529(8)	0.413(3)	-0.254(3)	HC(15)	-0.0582(9)	0.203(3)	-0.211(1)
HC(17)	0.1732(9)	0.015(3)	0.172(2)	HC(18)	0.2124(10)	-0.139(4)	0.242(2)
HC(19)	0.2337(13)	-0.328(5)	0.180(3)	HC(20)	0.2115(10)	-0.309(3)	0.049(2)
HC(21)	0.1706(8)	-0.176(4)	-0.031(2)	HC(22)	0.0779(7)	0.136(3)	-0.111(2)
HC(23)	0.0293(9)	0.027(3)	-0.191(2)	HC(24)	0.0215(11)	-0.208(4)	-0.186(2)
HC(25)	0.0623(10)	-0.318(4)	-0.099(2)	HC(26)	0.1058(10)	-0.213(4)	-0.007(2)
HC(1E)	0.1165(22)	0.495(8)	0.244(5)	HC(1E')	0.1635(15)	0.546(6)	0.216(3)
HC(2E)	0.1217(16)	0.648(6)	0.134(3)	HC(2E')	0.1397(11)	0.527(4)	0.106(2)
HC(2E'')	0.1002(22)	0.507(9)	0.083(5)				

^a Non-H atoms are numbered as shown in Fig. 2, H atoms are given the same designation as the non-H atom to which they are bonded preceded by a H. If more than one H is bonded to an atom, the second and third Hs are given ' and '' symbols, respectively.

Table 5

Important bond distances (Å) and angles (°) with e.s.d.'s for VIII·2Et₂O as labeled in Fig. 2

Mo–P	2.517(1)	P–Mo–C(1)	177.55(10)
Mo–C(1)	2.003(3)	P–Mo–C(2)	91.46(9)
Mo–C(2)	2.026(3)	P–Mo–C(3)	87.14(8)
Mo–C(3)	2.065(3)	P–Mo–C(4)	90.14(9)
Mo–C(4)	2.023(3)	P–Mo–C(5)	92.59(9)
Mo–C(5)	2.019(3)	C(1)–Mo–C(2)	88.33(14)
C(1)–O(1)	1.141(4)	C(1)–Mo–C(3)	90.43(13)
C(2)–O(2)	1.138(3)	C(1)–Mo–C(4)	90.30(14)
C(3)–O(3)	1.119(4)	C(1)–Mo–C(5)	89.93(14)
C(4)–O(4)	1.133(4)	C(2)–Mo–C(3)	91.88(14)
C(5)–O(5)	1.129(3)	C(2)–Mo–C(4)	174.17(13)
P–N(1)	1.661(2)	C(2)–Mo–C(5)	86.50(14)
P–C(6)	1.826(2)	C(3)–Mo–C(4)	93.80(14)
P–C(7)	1.827(3)	C(3)–Mo–C(5)	178.35(14)
N(1)–C(8)	1.460(3)	C(4)–Mo–C(5)	87.83(14)
C(8)–C(9)	1.514(4)	Mo–C(1)–O(1)	177.82(28)
C(9)–N(2)	1.473(3)	Mo–C(2)–O(2)	176.56(26)
N(2)–C(10)	1.280(3)	Mo–C(3)–O(3)	178.54(35)
C(16)–O(6)	1.292(3)	Mo–C(4)–O(4)	176.01(34)
Ni–N(2)	1.930(2)	Mo–C(5)–O(5)	178.72(29)
Ni–O(6)	1.829(2)	Mo–P–N(1)	113.02(8)
Mo–Ni	7.113(1)	Mo–P–C(6)	111.44(8)
		Mo–P–C(7)	117.16(7)
		P–N(1)–C(8)	124.01(19)
		N(1)–C(8)–C(9)	112.63(24)
		C(8)–C(9)–N(2)	112.56(23)
		C(9)–N(2)–C(10)	115.22(24)
		C(9)–N(2)–Ni	120.85(19)
		C(10)–N(2)–Ni	123.94(20)
		N(2)–Ni–O(6)	93.13(9)

contains a high spin Co²⁺, and the wavelengths of the three VIS-NIR absorptions indicate that the Co²⁺ is in an octahedral coordination environment [38]. These results are in agreement with the carbon-hydrogen analysis of the complex which indicates the presence of two water molecules which could serve as the axial ligands in an octahedral complex. The presence of the water molecules in IX is confirmed by an IR absorption at $\sim 3400\text{ cm}^{-1}$. Both VII and X have a single unpaired electron, as is expected for a d^9 Cu²⁺ ion, unfortunately their VIS-NIR spectra do not give any information as to the coordination environment of the Cu²⁺ ion.

X-Ray crystal structure of VIII·2Et₂O

The molecular structure of VIII·2Et₂O is shown in Fig. 2. Coordinates of the refined atoms are given in Table 4 and pertinent bond lengths and bond angles are given in Table 5. The Ni²⁺ ions of VIII occupy inversion centers in a manner similar to the Cu²⁺ ions in the VII·2THF [29]. In the crystal structure of VIII·2Et₂O, however, only one molecular conformation of the trinuclear complex is found, whereas in VII·2THF two conformers differing primarily in orientation about the Mo–P bond are observed. The conformation about the Mo–P bond in

Table 6
Significant torsion angles for VII·2THF and VIII·2Et₂O

Atom1	Atom2	Atom3	Atom4	Torsion angle (°)		
				VIIA ^a	VIIB ^a	VIII
C(2)	Mo	P	N(1)	161.7	−66.7	148.9
C(3)	Mo	P	N(1)	70.7	−158.4	57.1
C(4)	Mo	P	N(1)	−22.2	112.1	−36.7
C(5)	Mo	P	N(1)	−111.1	142.3	−124.6
C(2)	Mo	P	C(6)	41.9	53.1	26.9
C(2)	Mo	P	C(7)	−78.9	174.5	−93.5
Mo	P	N(1)	C(8)	176.7	−177.9	178.6
P	N(1)	C(8)	C(9)	−133.6	135.3	−142.4
N(1)	C(8)	C(9)	N(2)	66.7	−65.2	71.1
C(8)	C(9)	N(2)	M	83.4	−83.9	83.9

^a A signifies the molecule of VII at (0,0,0) and B signifies the molecule of VII at (1/2,1/2,0).

VIII·2Et₂O is similar to that of the molecule of VII·2THF located about 0, 0, 0 as illustrated by the torsion angles listed in Table 6.

The molecular centrosymmetry about the Ni²⁺ ion in the crystal necessitates a *trans* square planar arrangement of the salicylaldiminato-*N,O* ligands. The O(6)–Ni–N(2) angle of 93.13(9)° is slightly larger than those reported for the two independent molecules of VII·2THF (91.60(6) and 91.77(6)°) due to the larger ionic radius of the Ni²⁺ ion.

The non-tetrahedrally distorted square planar coordination of the Ni²⁺ by the salicylaldiminato-*N,O* ligands in VIII·2Et₂O is similar to that of the Cu²⁺ in VII·2THF. This type of configuration is unusual for bis(salicylaldiminato-*N,O*)Cu complexes with bulky *N*-substituents but is observed for bis(salicylaldiminato)Ni complexes with primary alkyl substituents on the imine N [39]. The lack of tetrahedral distortion appears to be due, at least in part, to symmetrical intramolecular stacking interactions between this group and the phenyl rings on P. The plane through atoms N(2), O(6) and Ni of the bis(salicylaldiminato-*N,O*)Ni chelate is nearly parallel to the plane through atoms C(7), C(22), C(23), C(24), C(25) and C(26) (dihedral angle of 17.8(1)°). The closest intermolecular contacts between the planes are made by Ni and C(22) (3.824(4) Å), Ni and C(23) (3.674(6) Å), Ni and C(24) (3.843(8) Å), O(6) and C(22) (3.776(4) Å), O(6) and C(23) (3.292(6) Å), O(6) and C(24) (3.811(7) Å) and N(2) and C(22) (3.662(4) Å). These types of interactions are common in crystals of aromatic compounds that contain either heteroatoms or polar substituents and in crystals of charge transfer complexes. The interactions are apparently due to dipole-induced dipole forces that involve a partial bond moment and a polarizable π -electron system [40].

The arrangement of the ligands about the molybdenum atoms in VIII·2Et₂O is best described as a slightly distorted octahedron similar to that observed in other (CO)₅Mo(P-donor ligand) complexes [41]. The dihedral angles formed by the three equatorial planes of four donor atoms are 90.1(1), 89.3(1) and 92.7(1)°. As previously observed in other complexes of the type (CO)_{6-n}M(P-donor ligand)_n (M = Cr, Mo; *n* = 1, 2), the M–C bond of the CO *trans* to the P-donor ligand is significantly shorter than are those *trans* to other CO ligands due to the poor π -acceptor abilities of the P-donor ligand.

The Mo–Ni distance of 7.113(1) Å in VIII · 2Et₂O is very close to the Mo–Cu distances of 7.078(1) and 7.079(1) Å in the two independent molecules of VII · 2THF. The metal–metal distances in these complexes are much longer than those observed for heterobimetallic complexes containing two bridging P-donor/salicylaldiminato or P-donor/diketonato ligands. The Mo–Ni distance in *trans*[*cis*-Mo(CO)₄(Ph₂-PNHCH₂CH₂N=CHC₆H₄-*o*-O)₂]Ni which has the same bridging ligands as those in VII and VIII is 5.697(1) Å [28] while the Pt–Cu distance in *cis*-PtCl₂(Pacac)₂Cu (Pacac = [*o*-diphenylphosphino)benzoyl]pinacolone), which has a two atom bridge between the two coordination sites, is 3.966(1) Å [23,24]. These comparisons demonstrate that both the number of atoms separating the coordination sites in the polyfunctional ligands and the number of ligands bridging the two metal centers have significant effects upon the metal–metal distances in the heteropolymetallic complexes.

Conclusions

Unusual heteropolymetallic complexes can be synthesized via the well known reactions of coordinated P-donor ligands. The sequential synthesis and complexation of the various coordination sites of the bridging ligand allows the coordination environment of the metals in the complexes to be precisely controlled. These reactions are quite general, and thus it should be possible to use the same sequence of reactions to synthesize similar complexes in which the metal centers, the chain length of the bridging ligand(s), and/or the Schiff base coordination site are systematically varied.

The single bridging ligand in the heterotrimetallic complexes in this study gives rise to two unusual features. The first is the stacking interactions between P-phenyl rings and the bis(salicylaldiminato)M groups which are observed in the solid state structures of the diphenylphosphino complexes, VII · 2THF and VIII · 2Et₂O. These interactions result in square planar coordination of the central metal ion, unusual for the Cu²⁺ ion, which are not observed in the solid state structure of a bimetallic Mo–Ni complex in which the metals are bridged by two of the phosphine-salicylaldiminato ligands. The second feature of interest is that the two different metals in the singly-bridged trimetallic complex are 1.4 Å further apart than are the metals in the doubly-bridged bimetallic complex. Both these features may be of significance to the catalytic properties of complexes similar to those discussed in this paper in which the Mo center is replaced by catalytically active group 9 or 10 metal centers.

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