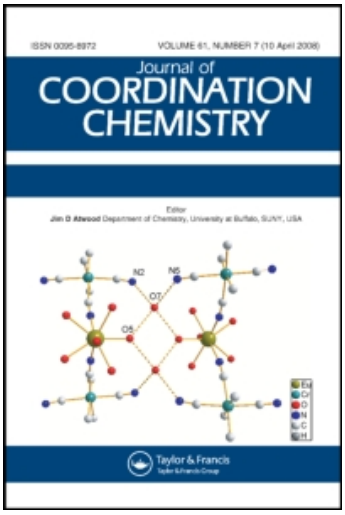

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PREPARATION AND CHARACTERIZATION OF TRIS(3,3-DIMETHYLBUTNYL)PHOSPHINE COMPLEXES OF GROUP VI METAL CARBONYLS

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The preparation and characterization of a series of compounds of the type $M(CO)_{6-n}L_n$; where M = Cr, n = 1 and M = Mo or W, n = 1,2, or 3 for $L = P[C{\equiv}CC(CH_3)_3]_3$ is reported. Infrared and phosphorus-31 magnetic resonance data for these complexes are discussed.

INTRODUCTION

A wide variety of alkynylphosphine metal complexes have been prepared recently.[1-4] The ligands, however, differ markedly in their mode of coordination, depending upon their structure and the substrate with which they are interacting. Here we report the preparation and characterization of tris(3,3-dimethylbutynyl)phosphine complexes of chromium, molybdenum and tungsten carbonyls, in which the phosphine ligand is acting as a two-electron donor with coordination through the phosphorus atom.

EXPERIMENTAL[5]

A nitrogen atmosphere was provided for all reactions, work-up steps and product storage. Ultraviolet irradiations were carried out using either an Engelhard-Hanovia 450-Watt or 550-Watt mercury ultraviolet lamp. The immersion lamp was placed in the water-cooled quartz center of the irradiation apparatus, irradiating outwards into a glass-enclosed, thin layer of solution. The solution was stirred magnetically and a nitrogen atmosphere was provided during the entire irradiation operation. All solvents were freshly distilled from an appropriate drying agent immediately before use, and deaerated with nitrogen.

Microanalyses (Table I) were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. Proton nmr spectra (Table II) were obtained by means of a Varian A-60D spectrometer. Phosphorus-31 nmr spectra were run at 40.5 MHz on a Varian XL-100 spectrometer assisted by a Varian 620-I computer. Infrared spectra (Table II) were determined using a Perkin-Elmer Model 621 grating spectrophotometer. Molecular weights were determined using a Hewlett-Packard Model 302B vapor phase osmometer.

The ligand L, tris(3,3-dimethylbutynyl)phosphine, $P[C{\equiv}CC(CH_3)_3]_3$, was prepared by a variation of a published procedure.[6] The intermediate lithium salt, 3,3-dimethylbutynyllithium, was prepared by the method of Reiff and Pant[6] but was not isolated. Improved yields of the ligand were obtained when, after the lithium salt was formed, the reaction mixture was cooled to −78°C and the appropriate amount of freshly distilled PCl_3 was added dropwise, as a solution in diethyl ether. The product was sublimed twice at 80-95°C/0.01 mm as a white crystalline solid onto a dry ice cooled finger, mp 84-85°C (lit., 83-84°C).[6] $Cr(CO)_4$(norb),[5,7] $Mo(CO)_4$(norb),[5,7] $Mo(CO)_3(CH_3CN)_3$,[8] $Mo(CO)_3(C_7H_8)$,[7] $W(COO)_4$(norb),[5,9] $W(CO)_3(CH_3CN)_3$,[8] and $W(CO)_3(C_7H_8)$[9] were prepared by published procedures.

The following materials were purchased from the indicated sources: $Cr(CO)_6$ and CH_3Li Alfa Inorganics Beverly, Mass.; 3,3-dimethylbutyne, Frinton Laboratories, S. Vineland, New Jersey.

Preparation of $Mo(CO)_5L$. A solution of 1.4 g (5.30 mmol) of $Mo(CO)_6$ in 100 ml of tetrahydrofuran was irradiated (450-Watt lamp) for 5½ hr. A 1.00 g (3.65 mmol) sample of the ligand was added and the yellow solution was stirred for 50 min at room temperature. Solvent was removed *in vacuo*

TABLE I
Physical properties and analytical data

Compound	Color	mp,[a] (°C)	% calcd C	% calcd H	% found C	% found H
$Cr(CO)_5L$	pale yellow	50-51	59.2	5.8	59.3	6.1
$Mo(CO)_5L$[b]	white	183-184 dec	54.0	5.3	54.5	5.6
$Mo(CO)_4L_2$	white	180-181	63.5	7.2	63.4	7.4
$Mo(CO)_3L_3$[c]	white	182-183	68.2	8.2	67.4	8.1
$W(CO)_5L$	pale yellow	106-107	46.2	4.6	46.1	4.7
$W(CO)_4L_2$	white	169-170	56.9	6.4	56.9	6.8
$W(CO)_3L_3$	pale yellow	186-187 dec	62.7	7.4	61.9	7.2

[a] Sealed tube, uncorrected.
[b] Calcd: P, 6.1. Found: P, 6.2.
[c] Molecular weight in benzene, Calcd: 1002. Found: 1054.

TABLE II
Infrared and proton nmr data

Compound	τ[a] $[C(CH_3)_3]$	$\nu(C\equiv C)$ (rel. int.)[b] cm^{-1}	$\nu(C\equiv O)$ (rel. int.)[b] cm^{-1}
L	8.68	2211(0.7) 2167(1.0)	
$Cr(CO)_5L$	8.70	2211(0.05) 2169(0.1)	2069(0.3) 1951(1.0) 1923(0.3)
$Mo(CO)_5L$	8.69	2209(0.1) 2169(0.2)	2080(0.3) 1956(1.0) 1931(sh)
$Mo(CO)_4L_2$	8.72[d]	2218(0.1) 2179(0.2)	2043(0.6) 1940(0.9) 1928(1.0) 1915(0.8)
$Mo(CO)_3L_3$	8.69[d]	2216(0.2) 2178(0.4)[c]	1969(1.0) 1888(1.0)[c]
$W(CO)_5L$	8.71	2213(0.1) 2173(0.2)[c]	2080(0.3) 1951(1.0) 1920(0.3)[c]
$W(CO)_4L_2$	8.71	2211(0.1) 2164(0.2)[c]	2032(0.5) 1935(0.8) 1919(1.0) 1914(0.9)[c]
$W(CO)_3L_3$	8.69	2208(0.2) 2169(0.4)	1963(1.0) 1880(1.0)

[a] CCl_4 solution relative to $Si(CH_3)_4$.
[b] CCl_4 solution.
[c] Hexane solution.
[d] A mixture of $Mo(CO)_4L_2$ and $Mo(CO)_3L_3$ gave two sharp singlets at τ8.72 and τ8.69 in CCl_4 solution (see experimental section).

leaving a mustard powder, which was placed in a sublimator. Unreacted $Mo(CO)_6$ (0.45 g, 1.79 mmol) was removed at 30-45°C/0.1 mm, and the white product (1.06 g, 58%) sublimed onto the dry ice cooled finger at 80-100°C/0.1 mm.

The residual mustard solid (0.70 g) was dissolved in hot hexane and filtered through a one inch layer of deaerated florisil to give a colorless filtrate, which upon cooling to −10°C yielded the disubstituted product $Mo(CO)_4L_2$ (0.16 g, 10%) mp 180-181°C.

Preparation of $Mo(CO)_4L_2$. A solution of 0.45 g (1.50 mmol) of bicycloheptadienetetracarbonylmolybdenum and 0.85 g (3.10 mmol) of the ligand in 75 ml of tetrahydrofuran was heated at reflux for 1 hr. Solvent was removed *in vacuo* and the pale tan solid was placed in a sublimator. Unreacted $Mo(CO)_6$ and unreacted ligand L were removed by heating up to 115°C. Attempts to sublime the product at 130°C resulted in signs of decomposition. The residue from the attempted sublimation was dissolved in hot hexane and was filtered immediately through a hot filter funnel. The filtrate was cooled to −78°C for 30 min to promote crystallization. Most of the supernatant liquid was removed before refiltration. The crystals were washed with 10 ml of cold pentane (−78°C) and dried *in vacuo* to give 0.74 g (65%) of product.

Preparation of $Mo(CO)_3L_3$. A solution of 0.50 g (1.85 mmol) of cycloheptatrienetricarbonylmolybdenum and 1.70 g (6.20 mmol) of the ligand in 50 ml of tetrahydrofuran was stirred for 16 hr at room temperature. Solvent was removed *in vacuo* and 0.20 g (0.73 mmol) of unreacted ligand recovered by sublimation at 90°C/0.01 mm from the reaction residue. The residue was dissolved in about 30 ml of hot hexane and filtered through a one inch layer of deaerated alumina. The yellow filtrate was cooled to −78°C to give 0.75 g of a light cream solid which was filtered off and washed with cold pentane (−78°C). Thin layer chromatography on alumina with hexane indicated two products (R_f 1.5 and R_f 2.5). Chromatography on deaerated alumina, eluting with hexane, gave initially a mixture and finally a pure product, believed to be *fac-*$Mo(CO)_3L_3$. The mixture comprised the di- and trisubstituted ligand complexes.

The alumina through which the hot hexane solution had been initially filtered was extracted with a further 50 ml of hot hexane. On cooling to −78°C, 0.11 g of pure *fac-*$Mo(CO)_3L_3$ was isolated as a white crystalline solid.

Molecular weight studies established *fac-*$Mo(CO)_3L_3$ as a trisubstituted complex (Calcd: 1002, Found: 1054) and the mixed product as a mixture of di- and trisubstituted ligand complexes (Found: 848). The fractions from the chromatography had successively increasing molecular weights until pure *fac-*$Mo(CO)_3L_3$ was eluted.

$Mo(CO)_3L_3$ was also prepared from $Mo(CO)_3(CH_3CN)_3$ in tetrahydrofuran.

Preparation of $W(CO)_5L$. A solution of 1.76 g (5.00 mmol) of $W(CO)_6$ in 75 ml of tetrahydrofuran was irradiated (550-Watt lamp) until the loss of about 1 1/2 equivalents of carbon monoxide was effected (*ca.* 45 min). A 1.30 g (4.75 mmole) sample of the ligand was added and the yellow solution was stirred for 50 min at room temperature. Solvent was removed *in vacuo* and the yellow residue was placed in a sublimator with a dry ice cooled finger. Samples of the sublimate were removed at 5-10°C temperature intervals from *ca.* 80°-125°C. Elemental analysis confirmed that the purest sample of pale yellow $W(CO)_5L$ (1.20 g) was obtained in the region from 120-125°C/0.015 mm.

Preparation of $W(CO)_4L_2$. A continuation of the sublimation from the above experiment to higher temperatures produced 0.70 g of pale yellow $W(CO)_4L_2$ at 147-165°C/0.015 mm. $W(CO)_4L_2$ was also prepared by reacting 0.26 g (0.67 mmol) of bicycloheptadienetetracarbonyltungsten and 0.31 g (1.20 mmol) of the ligand in 75 ml of tetrahydrofuran. The solution was stirred for 30 hr at room temperature. Solvent was removed *in vacuo* and unreacted ligand was sublimed from the residue as previously described. The product was obtained in about 65% yield by dissolving the residue in hot hexane, filtering through a 1/2 inch layer of deaerated alumina, and cooling the solution to −78°C. The white crystals were filtered off, washed with 5 ml of cold (-78°C) pentane, and dried *in vacuo.*

Preparation of $W(CO)_3L_3$. A solution of 0.13 g (3.50 mmol) of cycloheptatrienetricarbonyltungsten and 0.30 g (1.10 mmol) of the ligand in 30 ml of benzene was stirred for 13 hr. Solvent was removed at room temperature. The residue was chromatographed on deaerated alumina. Elution with hexane removed unreacted ligand and $W(CO)_4L_2$. A yellow band, containing $W(CO)_3L_3$, was eluted with a 50:50 benzene:hexane solution. Solvent was removed to yield 0.17 g (44%) of pure product.

Preparation of $Cr(CO)_5L$ A 0.8 g (3.6 mmol) sample of $Cr(CO)_6$ in 75 ml of tetrahydrofuran was irradiated (450-Watt lamp) for 16 hr. A 0.98 g (3.6 mmol) sample of the ligand was added and the yellow solution was stirred for 30 min. Solvent was removed *in vacuo* and any unreacted $Cr(CO)_6$ and ligand were removed by sublimation at 80-85°C/0.01 mm. The remaining yellow crystalline solid was shown to be pure $Cr(CO)_5L$, *ca.* 50% yield.

Attempted preparation of $Cr(CO)_4L_2$ and $Cr(CO)_3L_3$ Several attempts were made to synthesize these products, but in all cases only the monosubstitued product and excess ligand were isolated.

The preparation of $Cr(CO)_4L_2$ was first attempted *via* the bicycloheptadienetetracarbonylchromium complex. After refluxing with two equivalents of the ligand in tetrahydrofuran, unreacted phosphine and $Cr(CO)_5L$ were isolated.

A 0.5 g (2.45 mmol) sample of $Cr(CO)_6$ was irradiated (450-Watt lamp) in tetrahydrofuran until two equivalents of carbon monoxide were liberated (30 hr). Addition of 1.4 g (5.1 mol) of the ligand and stirring for 1 hr, resulted, after work-up, in the isolation of unreacted ligand and $Cr(CO)_5L$.

Similarly, an attempt to prepare $Cr(CO)_3L_3$ by irradiation gave only unreacted ligand and $Cr(CO)_5L$.

DISCUSSION

Only the monosubstituted chromium complex, $Cr(CO)_5L$, was prepared despite a number of attempts by different methods to prepare pure $Cr(CO)_4L_2$ and $Cr(CO)_3L_3$ (see Experimental).

The mono-, di-, and trisubstituted molybdenum complexes were prepared. $Mo(CO)_4L_2$ was isolated as a coproduct in the photochemical preparation of $Mo(CO)_5L$, as well as being prepared from $Mo(CO)_4$(norb). The infrared spectrum (Table II) of $Mo(CO)_4L_2$ in the carbonyl region shows the four carbonyl stretching modes predicted for *cis*-$Mo(CO)_4L_2$, based upon C_{2v} symmetry.[10]

The reaction of either $Mo(CO)_3(C_7H_8)$ or $Mo(CO)_3(CH_3CN)_3$ with three equivalents of the ligand at room temperature in THF gave a mixture of $Mo(CO)_4L_2$ and $Mo(CO)_3L_3$. Although $Mo(CO)_3L_3$ disproportionated to $Mo(CO)_4L_2$, a sample of pure *fac*-$Mo(CO)_3L_3$ was obtained by chromatography. The stereochemistry was assigned on the basis of the two strong carbonyl stretching frequencies observed in the infrared spectrum (Table II) that are expected for C_{3v} symmetry.[10,11]

$W(CO)_5L$ was prepared by the reaction of $W(CO)_5$(THF) with one equivalent of the phosphine ligand. A coproduct of this reaction was *cis*-$W(CO)_4L_2$. The preparation of *fac*-$W(CO)_3L_3$ was difficult because of its rapid disproportionation to $W(CO)_4L_2$, especially in solution. Although detectable (infrared spectrum) quantities of $W(CO)_3L_3$ were observed when $W(CO)_3(C_7H_8)$ and $W(CO)_3(CH_3CN)_3$ reacted with three equivalents of the ligand in THF, a more satisfactory method involved benzene as the reaction medium at room temperature.

The proton nmr spectral data of all the complexes and of the uncoordinated ligand are tabulated in Table II. Since the methyl protons are far removed from the coordinating metal and from the neighboring methyl protons, it is not surprising that all proton resonances appear to be essentially identical, within experimental error. However, a mixture of *cis*-$Mo(CO)_4L_2$ and *fac*-$Mo(CO)_3L_3$ did show two distinct, sharp singlets at 8.69τ and 8.72τ. This spectral pattern remained constant in deuterochloroform and in benzene solutions, although the chemical shifts varied with solvent. The difference between the chemical shifts of the methyl protons of *cis*-$Moo(CO)_4L_2$ and *fac*-$Mo(CO)_3L_3$, albeit small, indicates a subtle difference in the chemical environment of these apparently distant protons. This difference seems very unlikely to be due to any through-bond effect from the metal and/or the alkyne groups, but rather to a mild perturbation of the methyl protons by neighboring protons.

The infrared spectra (Table II) of the ligand and the complexes show both symmetric and antisymmetric $\nu(C\equiv C)$ frequencies. Recent papers[3,4] dealing with alkynylphosphine metal complexes have discussed, at length, the magnitude of the increase in the $\nu(C\equiv C)$ frequency upon going from the free ligand to various complexes of the ligand. This increase has been related to the degree of metal-phosphorus retrodative $d\pi$-$d\pi$ bonding, which in turn reduces the $d\pi$-$p\pi$ bonding between phosphorus and the acetylenic carbons. The observed changes in $\nu(C\equiv C)$ upon complexation of $P[C\equiv CC(CH_3)_3]_3$ for the compounds reported here are small in magnitude and show no obvious, systematic variation (after allowing for the fact that two different solvents were used for obtaining the solution infrared spectra).

The phosphorus-31 chemical shift data for the ligand and five of the complexes are given in Table

TABLE III
Phosphorus-31 nmr data

Compound	δ[a]	Δ[b]
L	+88.8	---
$Cr(CO)_5L$	+20.0	-68.8
$Mo(CO)_5L$	+49.6	-39.2
$W(CO)_5L$	+76.6[c]	-12.2
$Mo(CO)_4L_2$	+46.5	-42.3
$W(CO)_4L_2$	+70.4[d]	-18.4

[a]Chemical shifts are in ppm relative to 85% H_3PO_4; C_6D_6 solvent.
[b]Δ (coordination chemical shift) = δ complex – δ free ligand.
[c]$J_{^{183}W^{31}P}$ = 259 cps.
[d]$J_{^{183}W-^{31}P}$ = 262 cps.

III. The ligand chemical shift is +90 ppm, which is relatively large for a symmetrically substituted tertiary organophosphine. The chemical shifts and coordination chemical shifts of the complexes vary systematically in agreement with previous observations by Grim.[12,13] The chemical shifts of the complexed phosphorus atom are all downfield from the uncomplexed ligand. The two observed tungsten-phosphorus coupling constants are very similar: $W(CO)_5L$ = 259 cps and $W(CO)_4L_2$ = 261 cps. Following the views of Grim,[14] this would suggest that tris(3,3-dimethylbutynyl)phosphine is a poorer π-acceptor than triphenylphosphine ($J_{W-P}W(CO)_5P(C_6H_5)_3$ = 280 cps). This is not surprising since there is strong evidence from x-ray crystallographic data[15] that $d\pi$-$p\pi$ bonding exists between phosphorus and the alkynyl group or groups in alkynylphosphines.

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