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Synthesis of Mo(II) and W(II) Complexes with 1,1-Dithiolate Ligands. Improved Preparation of $W(CO)_3(PPh_3)_2Cl_2$

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The complexes $M(CO)_2(PPh_3)L_2$ [$M = Mo, W; L = S_2CNR_2, S_2COMe, S_2P(OEt)_2$] *have been prepared by a halide replacement reaction of* $M(CO)_3(PPh_3)_2Cl_2$ *with the appropriate ligand. The routine synthesis of the tungsten complexes was made possible by the development of an improved method for the preparation of* $W(CO(_3(PPh_3)_2Cl_2$. *Reaction of* $M(CO)_3(PPh_3)_2Cl_2$ *with excess* $HS_2P(i\text{-}Pr)_2$ *and with one mole of* $HS_2P(OEt)_2$ *gives* $M(CO)_2(PPh_3)_2LCl$ *which have been shown to be 1:1 electrolytes in methanol and non-conductors in 1,2-dichloroethane.*

Introduction

Recently we reported [1, 2] the reactions of the Mo(II) complexes $Mo(CO)_2L_2$ [$L = S_2CNEt_2$, $S_2P(i\text{-}Pr)_2$] with acetylenes and described the unusual spectral properties of the products, $Mo(CO)(R\text{-}C_2\text{-}R')L_2$ and $Mo(R\text{-}C_2\text{-}R')_2L_2$. In an attempt to extend these studies to other similar ligand systems and to the analogous W(II) complexes, we have synthesized a number of complexes of the form $M(CO)_2(PPh_3)L_2$ and $M(CO)_2(PPh_3)_2LCl$ (L = 1,1-dithiolate ligand; M = Mo, W). The complexes $Mo(CO)_2(PPh_3)(S_2CNR_2)_2$ (R = Me, Et, n-Pr) were previously reported [3] by Colton and Rose and we have used a modification of their method for the syntheses involving other ligands. The starting material for the W(II) complexes, $W(CO)_3(PPh_3)_2Cl_2$, was also previously reported [4] by Colton and coworkers, but we found it necessary to develop a more reliable, higher yield synthesis of this compound. This report describes the improved and extended synthetic methods and gives spectral data for the new complexes.

Experimental

All reactions were carried out under an argon atmosphere using standard techniques. All solvents were dried over molecular sieves and degassed prior to use. Infrared spectra were recorded as KBr discs on a Beckman IR20A spectrophotometer and UV-visible spectra on a Cary 118C instrument. Conductivity measurements were made using a Radiometer instrument. Elemental analyses for CHN were determined in this laboratory using either a Hewlett–Packard 185 or a Perkin–Elmer 240 instrument. The complex $Mo(CO)_3(PPh_3)_2Cl_2$ was prepared by the literature [5] method. Yields and elemental analytical data for all complexes are given in Table I.

Preparation of $W(CO)_3(Ph_3)_2Cl_2$

Chlorine (45 ml) was condensed (acetone/CO_2) into a Schlenk tube containing $W(CO)_6$ (5.0 g) and the resulting slurry was stirred at –78 °C for 40 min. Keeping the reaction vessel at –78 °C, the chlorine was evaporated *in vacuo* into a trap cooled to –196 °C, and PPh_3 (7.5 g) in CH_2Cl_2 (100 ml) was slowly added to the solid brown residue. After stirring for 15 min at –78 °C, the acetone/CO_2 bath was removed and the reaction mixture was allowed to warm to room temperature. The yellow solid $W(CO)_3(PPh_3)_2Cl_2\cdot CH_2Cl_2$ which precipitated was isolated by filtration, washed with acetone and diethylether, and dried *in vacuo*. The yield was 8.0 g, 65%.

Preparation of $M(CO)_2(PPh_3)L_2$

$M(CO)_3(PPh_3)_2Cl_2$ (0.70 mmol) was suspended in CH_2Cl_2 (35 ml), a solution of the ligand (1.5 mmol) in MeOH (35 ml) was slowly added, and the reaction mixture stirred for 15 min at room temperature. With $HS_2P(OEt)_2$, concentration of the reaction mixture under vacuum resulted in the crystallization of the product, while for NaS_2CNR_2 and KS_2COMe the reaction mixture was evaporated to dryness under vacuum and the residue extracted with CH_2Cl_2. After evaporation of the extracts to dryness under vacuum, addition of diethylether gave a solid product which was isolated by filtration, washed with diethylether and dried *in vacuo*.

Preparation of $M(CO)_2(PPh_3)_2[S_2P(i\text{-}Pr)_2]Cl$

$M(CO)_3(PPh_3)_2Cl_2$ (0.70 mmol) was suspended in CH_2Cl_2 (35 ml) and a solution of $HS_2P(i\text{-}Pr)_2$ (1.5 mmol) in MeOH (20 ml) was slowly added. After

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TABLE I. Yield and Elemental Analytical Data[a].

Compound	Yield	C	H	N
$Mo(CO)_2(PPh_3)(S_2CNMe_2)_2$	79%	47.6 (47.7)	4.79 (4.12)	3.95 (4.28)
$W(CO)_2(PPh_3)(S_2CNMe_2)_2$	93%	42.3 (42.0)	3.73 (3.64)	3.72 (3.77)
$Mo(CO)_2(PPh_3)(S_2CNEt_2)_2$	82%	50.2 (50.7)	5.24 (4.93)	3.61 (3.94)
$W(CO)_2(PPh_3)(S_2CNEt_2)_2$	93%	44.6 (45.1)	4.44 (4.39)	3.43 (3.51)
$Mo(CO)_2(PPh_3)[S_2CN(n\text{-}Pr)_2]_2$[b]	51%	52.1 (53.3)	5.55 (5.61)	3.39 (3.65)
$W(CO)_2(PPh_3)[S_2CN(n\text{-}Pr)_2]_2$	78%	47.3 (47.8)	4.69 (5.04)	3.20 (3.28)
$Mo(CO)_2(PPh_3)[S_2P(OEt)_2]_2$	88%	43.1 (42.9)	4.45 (4.71)	–
$W(CO)_2(PPh_3)[S_2P(OEt)_2]_2$	71%	38.2 (38.5)	4.08 (4.01)	–
$Mo(CO)_2(PPh_3)(S_2COMe)_2$[c]	73%	47.3 (45.9)	3.39 (3.34)	–
$W(CO)_2(PPh_3)(S_2COMe)_2$	78%	39.9 (40.2)	2.90 (2.93)	–
$Mo(CO)_2(PPh_3)_2[S_2P(i\text{-}Pr)_2]Cl$	85%	58.7 (59.2)	5.07 (4.93)	–
$W(CO)_2(PPh_3)_2[S_2P(i\text{-}Pr)_2]Cl$	53%	54.2 (53.9)	4.78 (4.49)	–
$Mo(CO)_2(PPh_3)_2[S_2P(OEt)_2]Cl$	60%	55.4 (56.2)	4.36 (4.46)	–
$W(CO)_2(PPh_3)_2[P(OEt)_2]Cl$	27%	50.8 (51.1)	4.04 (4.06)	–
$W(CO)_3(PPh_3)_2Cl_2 \cdot CH_2Cl_2$	65%	50.7 (50.7)	3.39 (3.38)	–

[a] Found values with calcd values in parentheses. [b] Difficulty was encountered in obtaining consistent elemental analytical data for this compound. [c] Shown by infrared spectra and by elemental analysis to be a mixture of ~90% $Mo(CO)_2(PPh_3)(S_2COMe)_2$ and ~10% $Mo(CO)(PPh_3)_2(S_2COMe)_2$.

stirring at room temperature for 30 min, the reaction mixture was filtered and the filtrate evaporated to 10 ml. Addition of diethylether (40 ml) caused the crystallization of the product which was isolated by filtration, washed with diethylether and dried *in vacuo*.

Preparation of $M(CO)_2(PPh_3)_2[S_2P(OEt)_2]Cl$

A solution of $HS_2P(OEt)_2$ (0.65 mmol) in 1,2-dichloroethane (35 ml) was slowly added to a slurry of $M(CO)_3(PPh_3)_2Cl_2$ (0.65 mmol) in the same solvent (35 ml). After stirring at room temperature for 30 min, the orange–brown reaction mixture was filtered and the filtrate evaporated to dryness under vacuum. Trituration of the residue with diethylether, gave a pink solid which was isolated by filtration, washed with diethylether, and dried *in vacuo*.

Results and Discussion

Synthesis of Molybdenum Complexes

The reaction of $Mo(CO)_3(PPh_3)_2Cl_2$ with N,N-dialkyldithiocarbamates in CH_2Cl_2 was previously [3] shown to yield $Mo(CO)_2(PPh_3)(S_2CNR)_2)_2$ (R = Me, Et, $CH_2C_6H_5$) with chloride being replaced by the uninegative bidentate sulfur-donor ligands to form seven-coordinate Mo(II) complexes. Our interest in the reactivity [6] of these compounds prompted us to synthesize the known dithiocarbamate complexes and to extend the reactivity to methylxanthate and diethyldithiophosphate ligands (eq 1).

$$Mo(CO)_3(PPh_3)_2Cl_2 + 2\,L^- \rightarrow Mo(CO)_2(PPh_3)L_2 + PPh_3 + 2\,Cl^- + CO \qquad (1)$$

$L = S_2CNR_2, S_2COMe, S_2P(OEt)_2$

We have modified the literature [3] procedure slightly by carrying out the reaction in a 1:1 $MeOH/CH_2Cl_2$ medium instead of pure CH_2Cl_2. The MeOH solubilizes the ligand and significantly increases the reaction rate.

In an attempt to prepare analogous dithiophosphinate $S_2P(i\text{-}Pr)_2$ derivatives, we reacted $Mo(CO)_3(PPh_3)_2Cl_2$ with excess $HS_2P(i\text{-}Pr)_2$ under the above conditions, but did not obtain the desired complex. Instead, only one chloride was replaced by $^-S_2P(i\text{-}Pr)_2$ to yield a new type of compound, as shown in eq 2.

$$Mo(CO)_3(PPh_3)_2Cl_2 + HS_2P(i\text{-}Pr)_2 \rightarrow Mo(CO)_2(PPh_3)_2[S_2P(i\text{-}Pr)_2]Cl + CO + HCl \qquad (2)$$

We were then able to prepare the complex $Mo(CO)_2(PPh_3)_2[S_2P(OEt)_2]Cl$ by reaction of $Mo(CO)_3(PPh_3)_2Cl_2$ with a stoichiometric amount of $HS_2P(OEt)_2$. Unfortunately, reaction of $Mo(CO)_3(PPh_3)_2Cl_2$ with equimolar quantities of KS_2COMe and NaS_2CNMe_2 did *not* yield pure $Mo(CO)_2(PPh_3)_2LCl$ but instead gave mixtures of starting material, $Mo(CO)_2(PPh_3)L_2$, and possibly some $Mo(CO)_2(PPh_3)_2LCl$ as evidenced by the CO stretching region of the ir spectra of isolated solids. This result would seem to indicate that the rate of replacement of the second chloride by $^-S_2CNR_2$ or $^-S_2COMe$ is greater than replacement of the first, but the mechanism of the reaction, along with the reasons for the very different behavior of the various ligands, must await a kinetic study of these reactions.

TABLE II. Spectral Properties of the Complexes.

Compound	Infrared[a]	Visible[b]	
$Mo(CO)_2(PPh_3)(S_2CNMe_2)_2$	1940, 1850	705(28), 455sh(735)[c]	
$W(CO)_2(PPh_3)(S_2CNMe_2)_2$	1910, 1820	685(76), 480sh(872)[c]	
$Mo(CO)_2(PPh_3)(S_2CNEt_2)_2$	1945, 1860	705(175), 485(784)[c]	
$W(CO)_2(PPh_3)(S_2CNEt_2)_2$	1930, 1835	685(223), 490(1060)[c]	
$Mo(CO)_2(PPh_3)[S_2CN(n\text{-}Pr)_2]_2$	1945, 1860	705(181), 485(831)[c]	
$W(CO)_2(PPh_3)[S_2CN(n\text{-}Pr)_2]_2$	1925, 1830	685(206), 488(1060)[c]	
$Mo(CO)_2(PPh_3)[S_2P(OEt)_2]_2$	1955, 1875	685(42), 460(375)[c]	
$W(CO)_2(PPh_3)[S_2P(OEt)_2]_2$	1940, 1850	630(38), 475sh(444), 435(517)[c]	
$Mo(CO)_2(PPh_3)(S_2COMe)_2$	1960, 1870	470(899)[c]	
$W(CO)_2(PPh_3)_2(S_2COMe)_2$	1950, 1860	475(1425)[c]	
$Mo(CO)_2(PPh_3)[S_2P(i\text{-}Pr)_2]Cl$	1955, 1865	625(202), 500(253)[c]	565(545)[d]
$W(CO)_2(PPh_3)_2[S_2P(i\text{-}Pr)_2]Cl$	1940, 1835	625sh(206), 500(394)[c]	525(856)[d]
$W(CO)_2(PPh_3)_2[S_2P(OEt)_2]Cl$	1935, 1840	467(601)[c],	537(572)[d]
$Mo(CO)_2(PPh_3)_2[S_2P(OEt)_2]Cl$	1950, 1860	457(421)[c],	580(339)[d]
$Mo(CO)_2(PPh_3)_2Cl_2$	1975, 1895	563(511)[c]	

[a] Terminal C≡O stretching frequencies in cm^{-1}. [b] Peak positions in nm with molar absorptivity in parentheses. [c] 1,2-dichloroethane solution. [d] Methanol solution.

Synthesis of Tungsten Complexes

In order to prepare the analogous W(II) complexes, $W(CO)_3(PPh_3)_2Cl_2$ was needed as the starting material. This compound was known [4], but no yield data was given, and furthermore, the method was not appealing as a routine preparation since it involved the dropwise addition of liquid chlorine to solutions of $W(CO)_6$ followed by a complicated work-up procedure. We felt that reaction of the isolated solid $W(CO)_4Cl_2$ [prepared [7] by simple condensation of liquid chlorine onto $W(CO)_6$] with PPh_3 was a more promising route. However, the room temperature reaction of PPh_3 in CH_2Cl_2 with $W(CO)_4Cl_2$ produced only a small amount of $W(CO)_3(PPh_3)_2Cl_2$. We reasoned that the poor yield might be due to the thermal instability of $W(CO)_4Cl_2$ and therefore kept this compound at −78 °C during *both* the vacuum distillation of Cl_2 into a trap cooled to −196 °C and the slow addition of a solution of PPh_3 in CH_2Cl_2. Only at this point was the reaction mixture allowed to warm to room temperature when the precipitated solid was easily isolated under ambient conditions. This procedure resulted in consistently high yields of $W(CO)_3(PPh_3)_2Cl_2$ and is, in our hands at least, a significant improvement over the literature [4] method. This complex may be an important synthetic reagent in tungsten chemistry since we have found that it reacts readily not only with sulfur donor ligands (see below), but also with other ligand types such as acetylacetone, 8-quinolinol, and cysteine esters [8]. These latter reactions are at present under study in this laboratory.

After larger quantities of $W(CO)_3(PPh_3)_2Cl_2$ were made available by the above improved synthetic method, the halide replacement reactions of this complex with the 1,1-dithiolate ligands used above were attempted and found to be facile. Reaction with excess $HS_2P(OEt)_2$, KS_2COMe, and NaS_2CNR_2 (R = Me, Et, n-Pr) gave $W(CO)_2(PPh_3)L_2$ analogously to eq 1, while reaction with excess $HS_2P(i\text{-}Pr)_2$ gave $W(CO)_2(PPh_3)_2[S_2P(i\text{-}Pr)_2]Cl$ as in eq 2. As for the molybdenum system, reaction of an equimolar amount of $HS_2P(OEt)_2$ with $W(CO)_3(PPh_3)_2Cl_2$ gave $W(CO)_2(PPh_3)_2[S_2P(OEt)_2]Cl$ but mixtures were obtained when KS_2COMe and NaS_2CNMe_2 were reacted under these conditions.

Characterization of $M(CO)_2(PPh_3)L_2$

Infrared and visible spectral data for both molybdenum and tungsten complexes are given in Table II. Predictably the infrared spectra of all compounds contain two strong C≡O stretching frequencies. In general the frequencies of tungsten complexes are 20–30 cm^{-1} lower than their molybdenum analogs. This small, but consistent, shift indicates more back bonding in the tungsten complexes ans is probably a reflection of the general increase in transition metal basicity on going down a given group [9]. No attempt has been made to assign the visible spectra of the complexes $M(CO)_2(PPh_3)L_2$ and the data is presented only as an aid for future characterization.

Characterization of $M(CO)_2(PPh_3)_2LCl$

Infrared and visible spectral data are found in Table II. The infrared spectra are characterized by two strong C≡O stretching frequencies which are again lower in energy for the tungsten complex. Interestingly, the visible spectra of the complexes are very dependent on solvent with the number of peaks and/or peak positions being a function of whether

TABLE III. Molar Conductivity Data (in ohm^{-1} cm^2 mol^{-1}) for the Complexes $M(CO)_2(PPh_3)_2LCl$.

Compound	Λ_M in MeOH	Λ_M in 1,2-Dichloroethane
$Mo(CO)_2(PPh_3)_2[S_2P(OEt)_2]Cl$	97	1.8
$W(CO)_2(PPh_3)_2[S_2P(OEt)_2]Cl$	78	0.3
$Mo(CO)_2(PPh_3)_2[S_2P(i\text{-}Pr)_2]Cl$	76	1.0
$W(CO)_2(PPh_3)_2[S_2P(i\text{-}Pr)_2]Cl$	72	1.0

methanol or 1,2-dichloroethane was used. This spectral difference suggested that in the more polar methanol the species present was the ionic complex $[M(CO)_2(PPh_3)_2L]^+Cl^-$, containing a six-coordinate M(II) cation, while in less polar 1,2-dichloroethane, the chloride remained coordinated. Indeed, the visible spectrum of $Mo(CO)_2(PPh_3)_2Cl_2$ (Table II) [indicated by X-ray crystallography [10] to be a six-coordinate monomer of Mo(II)] is very similar to the spectra of $Mo(CO)_2(PPh_3)_2LCl$ [L = $S_2P(OEt)_2$, $S_2P(i\text{-}Pr)_2$] in methanol. Final proof for the ionization theory comes from the measurement of the molar conductivity of the compounds in both solvents. In methanol, the values of 70–100 ohm^{-1} cm^2 mol^{-1} for *ca.* 10^{-3} *M* solutions of $M(CO)_2(PPh_3)_2LCl$ are close to the accepted [11] range of 80–115 ohm^{-1} cm^2 mol^{-1} for 1:1 electrolytes in that solvent. The molar conductivities of these compounds in 1,2-dichloroethane are very low and showed the species to be nonelectrolytes in this solvent. The slightly higher value for $Mo(CO)_2(PPh_3)_2[S_2P(OEt)_2]Cl$ may indicate that it is slightly ionized even in 1,2-dichloroethane.

The species $[M(CO)_2(PPh_3)_2L]^+$ [M = Mo, W; L = $S_2P(OEt)_2$, $S_2P(i\text{-}Pr)_2$] are formal 16-electron systems whose reactivity is potentially interesting since the complexes might be expected to add a variety of 2-electron donor reagents in order to attain the stable 18-electron configuration. Studies based on this theory are currently in progress.

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