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Syntheses and reactivity of molybdenum complexes containing the diphenylphosphinodithioformato ligand

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Abstract

Treatment of $[Et_4N][Mo(CO)5(PPh_2)]$ (**1**) with CS_2 afforded $[Et_4N][Mo(CO)_5(PPh_2CS_2)]$ (**3**) which was also synthesized from the reaction of $Mo(CO)_5(CH_3CN)$ with $[Et_4N][PPh_2CS_2]$ (**2**). In complex **3**, the diphenylphosphinodithioformato ligand, $PPh_2CS_2^-$, coordinated to the molybdenum through the phosphorus atom. The reactions of **3** with various alkyl halides yielded the neutral complexes $Mo(CO)_5[PPh_2(CS_2R)]$ ($R = C_2H_5$, C_2H_4OH, C_3H_5, **4**–**6**). Acylation of **3** with 1-naphthoyl chloride $[C_{10}H_7C(O)Cl]$ gave the complex $Mo(CO)_5[PPh_2(CS_2COC_{10}H_7)]$ (**7**) with moderate yield. Alkylation and acylation reactions occurred at the sulfur atom. Complex **3** reacted with CH_2I_2 to give the dinuclear complex $[Mo(CO)_5(PPh_2CS_2)]_2(\mu\text{-}CH_2)$ (**8**) in which the two metal atoms are bridged by the bidentate phosphorus ligand. Decarbonylation of **3** in CH_3CN produced an anionic product which was identified as $[Et_4N][Mo(CO)_4(PPh_2CS_2)]$ (**9**). The $PPh_2CS_2^-$ ligand of **9** bound to the metal center through both the phosphorus and one of the sulfur atoms. All of the complexes are identified by spectroscopic methods.

Keywords: Diphenylphosphinodithioformato ligand; Molybdenum complex; Alkylation, acylation and decarbonylation reactions

1. Introduction

Although the dithiocarbamato ligands [1], $R_2NCS_2^-$, have attracted considerable attention, little effort has been directed toward investigating the analogous dialkylphosphinodithioformato ligands, $R_2PCS_2^-$. Until now, only a few well-characterized $Ph_2PCS_2^-$ complexes of early transition metals such as Zr [2] and W [3] were reported, of which, this ligand coordinates to metal centers through the two S atoms or the P and S atoms by chelation, or the simple P-coordination. We were interested in the $Ph_2PCS_2^-$ and Ph_2PCS_2R complexes of W(0) which brought about some novel chemistry such as unprecedented monodentate P-coordination mode [3a], sulfur-assisted cyclization reaction [3b], phosphine transfer reaction, C=S π-coordination in Pd [3c] and intermolecular cyclization forming 6a-thiathiophthen [3d]. In the context of our previous studies, we extended the research to the syntheses and reactivity of molybdenum complexes with the $Ph_2PCS_2^-$ ligand.

2. Experimental

2.1. Materials

All manipulations were performed under nitrogen using vacuum-line, drybox, and standard Schlenk techniques. NMR spectra were recorded on a Bruker AC-200, or on a Bruker AM-300 WB FT-NMR spectrometer and are reported in units of δ with residual protons in the solvent as an internal standard ($CDCl_3$, δ 7.24; CD_3CN, δ 1.93; C_6D_6, δ 7.15; C_2D_6CO, δ 2.04). IR spectra were measured on a

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Perkin–Elmer 983 instrument and were referenced to polystyrene standard, using cells equipped with calcium fluoride windows. Mass spectra were recorded on a Jeol SX-102A spectrometer. Solvents were dried and deoxygenated by refluxing over the appropriate reagents before use. *n*-Hexane, diethyl ether, THF and benzene were distilled from sodium-benzophenone. Acetonitrile and dichloromethane were distilled from calcium hydride, and methanol from magnesium. All other solvents and reagents were of reagent grade and were used as received. $Mo(CO)_6$, allyl bromide and $KPPh_2$ were purchased from Strem, Merck and Aldrich, respectively. CS_2, *n*-BuLi, Et_4NBr, C_2H_5I, IC_2H_4OH, C_3H_5Br and CH_2I_2 were purchased from Janssen. The compound $[Et_4N][PPh_2(CS_2)]$ [3e] and $Mo(CO)_5(PPh_2H)$ [3f] were prepared according to the literature method. Elemental analyses were carried out at the Regional Center of Analytical Instrument located at the National Taiwan University.

2.2. Preparation of $[Et_4N][Mo(CO)_5(PPh_2)]$ (**1**)

To a flask containing $Mo(CO)_5(PPh_2H)$ (0.633 g, 1.5 mmol) and Et_4NBr (0.315 g, 1.5 mmol) in THF, *n*-BuLi (1 ml, 1.6 mmol) was added at 0°C. The solution was stirred for 5 min and the solvent was removed under vacuum. MeOH (15 ml) was added to the flask and the solution was stored at −18°C for 12 h to give yellow precipitates. These precipitates were filtered, washed with diethyl ether (2 × 10 ml) and then dried under vacuum to give **1** (0.77 g) as yellow powder in 93% yield. Spectroscopic data for **1**: IR (CH_2CI_2): ν_{CO} 2070(m), 1910(vs) cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 1.18 (tt, 12H, CH_3, $J_{N-H} = 1.87$ Hz, $J_{H-H} = 7.30$ Hz), 3.18 (q, 8H, CH_2, $J_{H-H} = 7.30$ Hz), 7.47 (m, 6H, Ph), 7.67 (m, 4H, Ph); ^{13}C-NMR (CD_3CN): δ 7.6 (s, CH_3), 52.9 (s, CH_2), 128.2 (d, *meta*-C of Ph, $J_{P-C} = 9.0$ Hz), 131.5 (s, *para*-C of Ph), 133.0(d, *ortho*-C of Ph, $J_{P-C} = 9.7$ Hz), 134.6 (d, *ipso*-C of Ph, $J_{P-C} = 34.6$ Hz), 205.7 (d, *cis*-CO, $J_{P-C} = 9.8$ Hz), 210.0 (d, $J_{P-C} = 25.8$ Hz, *trans*-CO); MS (FAB, NBA): *m*/*z* 681 ($M^+ + Et_4N$); Anal. Calc. for $C_{25}H_{30}NO_5PMo$ (551.41) C: 54.45, H: 5.48, N: 2.54. Found C: 54.35, H: 5.42, N: 2.25.

2.3. Preparation of $[Et_4N][Mo(CO)_5(PPh_2CS_2)]$ (**3**)

Method A: a CH_2Cl_2 solution (5 ml) of $Mo(CO)_5(CH_3CN)$ (0.277 g, 1.0 mmol) was added slowly at room temperature to a CH_2Cl_2 solution (20 ml) of $[Et_4N][PPh_2CS_2]$ (**2**) (0.391 g, 1.0 mmol). The solution was stirred for 1 h. The reaction was monitored by ^{31}P-NMR. After complete disappearance of the ^{31}P resonance of **2**, dichloromethane was removed under vacuum to give red–brown powder. The crude product was recrystallized from a 1:1 CH_2CI_2/MeOH solution to give a microcrystalline complex **3** (0.53 g, 84%). Method B: to a THF solution of **1** (0.551 g, 1.0 mmol), CS_2 (0.1 ml, 1.6 mmol) was added at room temperature. The color changed from bright yellow to red immediately accompanied with the formation of some red precipitates. The solution was filtered and the precipitates were washed with *n*-hexane (2 × 10 ml) to give a red powder 3 (0.55 g) in 87% yield. Spectroscopic data for **3**: IR (KBr): ν_{CO} 2065(s), 1979(m), 1949(vs), 1909 (vs) cm^{-1}, ^{31}P-NMR ($CDCl_3$): δ 69.8; H-NMR ($CDCl_3$): δ 1.18 (tt, 12H, CH_3, $J_{N-H} = 1.87$ Hz, $J_{H-H} = 7.30$ Hz), 3.15 (q, 8H, CH_2, $J_{H-H} = 7.30$ Hz), 7.35 (m, 6H, Ph), 7.66 (m, 4H, Ph); ^{13}C-NMR (CD_3CN): 0 7.6 (s, CH_3), 52.9 (s, CH_2), 128.3 (d, *meta*-C of Ph, $J_{P-C} = 9.8$ Hz), 129.9 (s, *para*-C of Ph), 134.4 (d, *ortho*-C of Ph, $J_{P-C} = 9.8$ Hz), 141.0 (d, *ipso*-C of Ph, $J_{P-C} = 34.2$ Hz), 204.8 (d, *cis*-CO, $^2J_{P-C} = 7.5$ Hz), 209.7 (d, *trans*-CO, $J_{P-C} = 25.5$ Hz), 235.7 (s, CS_2); MS (FAB, NBA): *m*/*z* 759 ($M^+ + Et_4N$), 703 ($M^+ + Et_4N$–2CO); Anal. Calc. for $C_{26}H_{30}NO_5PS_2Mo$ (627.56) C: 49.76, H: 4.82, N: 2.23. Found C: 49.74, H: 4.85, N: 2.22.

2.4. Preparation of $Mo(CO)_5[PPh_2(CS_2C_2H_5)]$ (**4**)

C_2H_5I (0.01 ml, 1.0 mmol) was added to a solution of **3** (0.627 g, 1.0 mmol) in CH_2Cl_2 (20 ml) and the mixture was stirred at room temperature for 1 min. The solvent was removed under vacuum and the residue was extracted with *n*-hexane (2 × 10 ml), and the extracts were filtered through celite. The filtrate was concentrated to ca. 5 ml and cooled to −18°C for 12 h to give the red crystalline product $Mo(CO)_5[PPh_2(CS_2C_2H_5)]$ (**4**) (0.45 g, 85%). Spectroscopic data for **4**: IR (CH_2Cl_2): ν_{CO} 2074(m), 1940(vs) cm^{-1}; ^{31}P-NMR ($CDCl_3$): δ 75.6; ^{1}H-NMR ($CDCl_3$): δ 1.32 (t, 3H, CH_3, $J_{H-H} = 7.50$ Hz), 3.29 (q, 2H, CH_2 $J_{H-H} = 7.50$ Hz), 7 47 (m, 6H, Ph), 7.67 (m, 4H, Ph); ^{13}C-NMR ($CDCl_3$): δ 11.8 (s, CH_3), 32.0 (s, CH_2), 128.4 (d, *meta*-C of Ph, $^3J_{P-C} = 9.6$ Hz), 130.8 (s, *para*-C of Ph), 133.6 (d, *ortho*-C of Ph, $^2J_{P-C} = 12.4$ Hz), 134.1 (d, *ipso*-C of Ph, $J_{P-C} = 31.9$ Hz), 205.4 (d, *cis*-CO, $J_{P-C} = 8.3$ Hz), 210.1 (d, *trans*-CO, $J_{P-C} = 26.3$ Hz), 238.9 (d, $J_{P-C} = 4.8$ Hz, CS_2); MS (FAB, NBA): *m*/*z* 528 (M^+), 499 ($M^+ - C_2H_5$), 471 ($M^+ - C_2H_5 - CO$), 443 ($M^+ - C_2H_5 - 2CO$), 415 ($M^+ - C_2H_5 - 3CO$), 387 ($M^+ - C_2H_5 - 4CO$), 359 ($M^+ - C_2H_5 - 5CO$). Anal. Calc. for $C_{20}H_{15}O_5PS_2Mo$ (526.37) C: 45.63, H: 2.87. Found C: 45.60, H: 2.85.

2.5. Preparation of $Mo(CO)_5[PPh_2(CS_2C_2H_4OH)]$ (**5**)

The synthesis and work-up were similar to those used in the preparation of complex **4**. The pure complex $Mo(CO)_5[PPh_2(CS_2C_2H_4OH)]$ (**5**) as the red microcrystalline solid was isolated in 90% yield. Spectroscopic data for **5**: IR (CH_2CI_2): ν_{CO} 2073(m), 1984(m), 1943(vs) cm^{-1}; ^{31}P-NMR ($CDCl_3$): δ 77.4; ^{1}H-NMR

($CDCl_3$): δ 3.30 (t, 2H, SCH_2, $J_{H-H} = 6.12$ Hz), 3.53 (t, 2H, CH_2OH, $J_{H-H} = 6.12$ Hz), 7.46 (m, 6H, Ph), 7.64 (m, 4H, Ph); ^{13}C-NMR ($CDCl_3$): δ 39.9 (s, SCH_2), 59.8 (s, CH_2OH), 128.5 (d, *meta*-C of Ph, $J_{P-C} = 13.5$ Hz), 131.1 (s, *para*-C of Ph), 133.8 (d, *ortho*-C of Ph, $J_{P-C} = 17.3$ Hz), 134.3 (d, *ipso*-C of Ph, $J_{P-C} = 38.8$ Hz), 205.4 (d, *cis*-CO, $J_{P-C} = 9.1$ Hz); 239.7 (s, CS_2); MS (FAB, NBA): m/z 544 (M^+), 516 ($M^+ - CO$), 460 ($M^+ - 3CO$), 432 ($M^+ - 4CO$), 404 ($M^+ - 5CO$). Anal. Calc. for $C_{20}H_{15}O_6PS_2Mo$ (542.37) C: 44.29, H: 2.79. Found C: 44.25, H: 2.85.

2.6. Preparation of $Mo(CO)_5[PPh_2(CS_2C_3H_5)]$ (6)

The synthesis and work-up were similar to those used in the preparation of complex **4**. The pure complex $Mo(CO)_5[PPh_2(CS_2C_3H_5)]$ (**6**) as the red microcrystalline solid was isolated in 85% yield. Spectroscopic data for **6**: IR (CH_2CI_2): ν_{CO} 2073(m), 1985(m), 1946(vs) cm^{-1}; ^{31}P-NMR ($CDCl_3$): δ 76.0; ^{1}H-NMR ($CDCl_3$): δ 3.93 (d, 2H, SCH_2, $J_{H-H} = 6$ 99 Hz), 5.18, 5.28 (d, 2H, $=CH_2$, $J_{H-H} = 9$ 99 Hz), 5.78 (m, 1H, CH=), 7.46 (m, 6H, Ph), 7.67 (m, 4H, Ph); ^{13}C-NMR ($CDCl_3$): 0 41.5 (s, SCH_2), 120.5 (s, CH=), 128.5 (d, *meta*-C of Ph, $J_{P-C} = 9.8$ Hz), 129.6 (s, $=CH_2$), 130.8 (s, *para*-C of Ph), 133.7 (d, *ortho*-C of Ph, $J_{P-C} = 12.4$ Hz), 134.9 (d, *ipso*-C of Ph, $J_{P-C} = 38.8$ Hz), 205.4 (d, *cis*-CO, $J_{P-C} = 8.4$ Hz), 210.0 (d, *trans*-CO, $J_{P-C} = 25.5$ Hz), 238.2 (s, CS_2); MS (FAB, NBA): m/z 540 (M^+), 512 ($M^+ - CO$), 456 ($M^+ - 3CO$), 428 ($M^+ - 4CO$), 400 ($M^+ - SCO$), 359 ($M^+ - 5CO - C_3H_5$). Anal. Calc. for $C_{21}H_{15}O_5PS_2Mo$ (538.38) C: 46.85, H: 2.81. Found C: 46.82, H: 2.87.

2.7. Preparation of $Mo(CO)_5[PPh_2(CS_2OCC_{10}H_7)]$ (7)

The synthesis and work-up were similar to those used in the preparation of complex **4**. The pure complex $Mo(CO)_5[PPh_2(CS_2OCC_{10}H_7)]$ (**7**) as the red microcrystalline solid was isolated in 46% yield. Complex **7** is air and moisture sensitive and elemental analysis was not obtained. Spectroscopic data for **7**: IR (CH_2Cl_2): ν_{CO} 2073(m), 1976(m), 1943(vs), 1726(vs) cm^{-1}; ^{13}P-NMR ($CDCl_3$): δ 775; ^{1}H-NMR ($CDCl_3$): δ 7.46–7.67 (m, 17H, Ph); ^{13}C-NMR ($CDCl_3$): δ 128.5–134.9 (m, C of Ph), 170.0 (s, SCO), 207.4 (d, *cis*-CO, $J_{P-C} = 8.4$ Hz), 211.0 (d, *trans*-CO, $J_{P-C} = 25.5$ Hz), 238.4 (s, CS_2); MS (FAB, NBA): m/z 654 (M^+).

2.8. Preparation of $[Mo(CO)_5(PPh_2CS_2)]_2(\mu\text{-}CH_2)$ (8)

CH_2I_2 (0.1 ml, 3.0 mmol) was added slowly to a solution of 3 (0.627 g, 1.0 mmol) in 20 ml of CH_2Cl_2 at room temperature and the solution was stirred for 5 min. The solvent was removed under vacuum and the residue was extracted with *n*-hexane (2×10 ml), and the extract was filtered through celite. The filtrate was concentrated to 5 ml and stored at -18°C for 12 h to give the red–brown crystalline product $[Mo(CO)_5(PPh_2CS_2)]_2(\mu\text{-}CH_2)$ (**8**) (0.41 g, 82%). Spectroscopic data for **8**: IR (CH_2Cl_2): ν_{CO} 2074(m), 1985(m), 1945(vs) cm^{-1}; ^{31}P-NMR ($CDCl_3$): δ 77.0; ^{1}H-NMR ($CDCl_3$): δ 4.99 (s, 2H, CH_2), 7.40–7.66 (m, 20H, Ph); ^{13}C-NMR ($CDCl_3$): δ 42.4 (s, CH_2), 128.5 (d, *meta*-C of Ph, $J_{P-C} = 8.3$ Hz), 131.3 (s, *para*-C of Ph), 133.6 (d, *ortho*-C of Ph, $J_{P-C} = 11.8$ Hz), 134.3 (d, *ipso*-C of Ph, $J_{P-C} = 46.0$ Hz), 205.2 (d, *cis*-CO, $J_{P-C} = 6.5$ Hz), 209.2 (d, *trans*-CO, $J_{P-C} = 25.5$ Hz), 237.6 (s, CS_2); MS (FBA, NBA): m/z 1010 (M^+), 786 ($M^+ - 8CO$), 758 ($M^+ - 9CO$), 730 ($M^+ - 10CO$); Anal. Calc. for $C_{37}H_{22}O_{10}P_2S_4Mo_2$ (1008 65) C: 44.06, H: 2.20. Found C: 44.00, H 2.27.

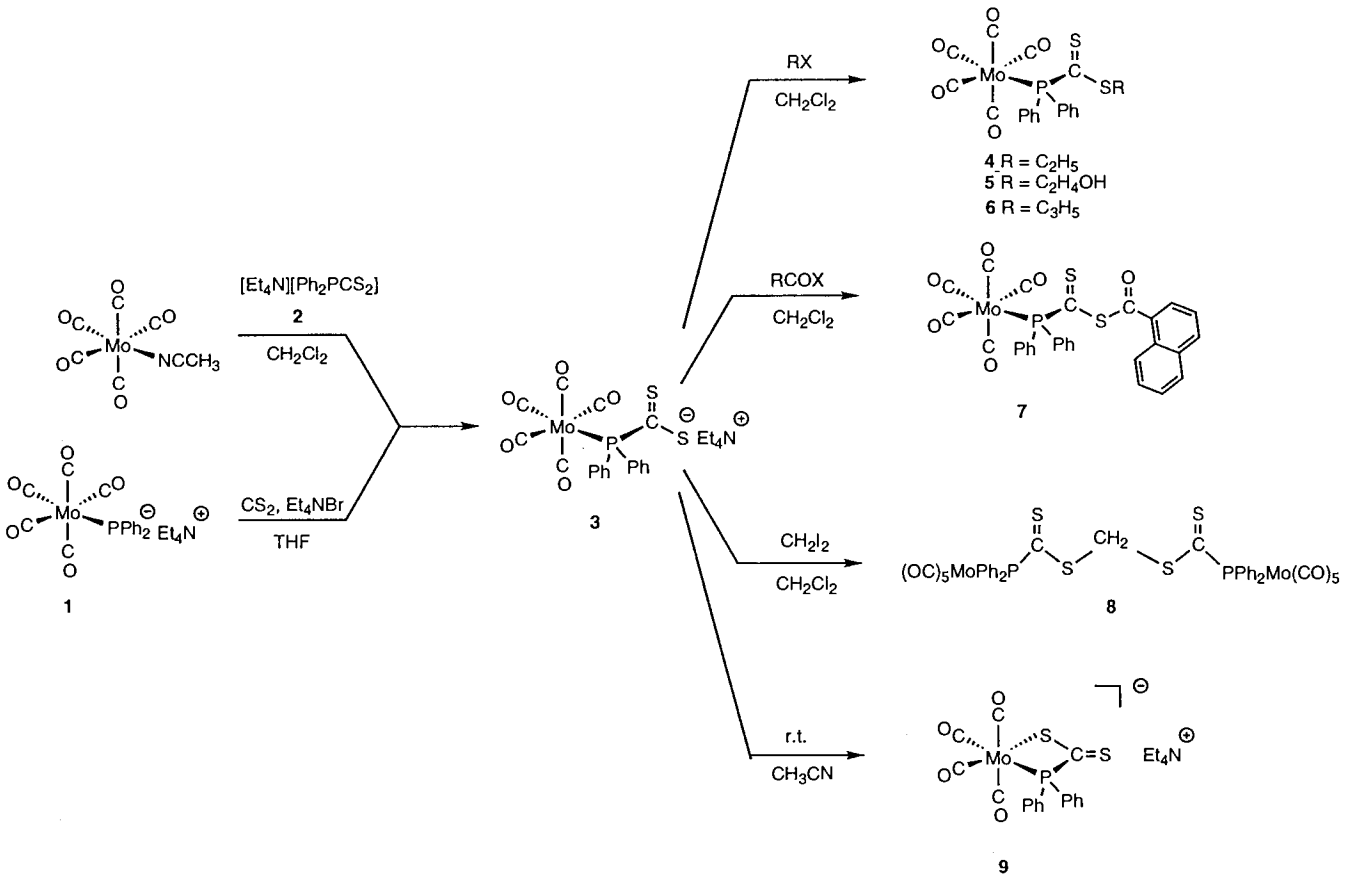
2.9. Preparation of $[Et_4N][Mo(CO)_4(PPh_2CS_2)]$ (9)

Compound **3** (0.627 g, 1.0 mmol) was dissolved in 10 ml of CH_3CN. The solution was stirred at room temperature and the reaction monitored by IR spectra. After stirring for 10 min, and IR spectrum indicated that the starting material was completely consumed. The solution was cooled and the solvent was removed in vacuum. Recrystallization using a cold 1:1 *n*-hexane/CH_2CI_2 to give the red crystalline product **9** (0.42 g, 70%). Spectroscopic data for **9**: IR (CH_2Cl_2): ν_{CO} 2009(m), 1893(vs), 1865(sh), 1827(s) cm^{-1}; ^{31}P-NMR ($CDCl_3$): δ 38.9; ^{1}H-NMR ($CDCl_3$): δ 1.18 (tt, 12H, CH_3, $J_{N-H} = 1.87$, $J_{H-H} = 7.30$ Hz), 3.15 (q, 8H, NCH_2, $J_{H-H} = 7.30$ Hz), 7.47 (m, 6H, Ph), 7.69 (m, 4H, Ph); ^{13}C-NMR ($CDCl_3$): δ 7.6 (s, CH_3), 52.9 (s, NCH_2), 129.0 (d, *meta*-C of Ph, $J_{P-C} = 8.3$ Hz), 130.9 (s, *para*-C of Ph), 133.8 (d, *ortho*-C of Ph, $J_{P-C} = 14.6$ Hz), 136.5 (d, *ipso*-C of Ph, $J_{P-C} = 21.8$ Hz), 211.0, 212.2 (*cis*-CO), 222.7 (d, *trans*-CO, $J_{P-C} = 28.9$ Hz), 238.1 (s, CS_2); MS (FAB, NBA): m/z 731 ($M^+ + Et_4N$), 703 ($M^+ + Et_4N - CO$); Anal. Calc. for $C_{25}H_{30}NO_4PS_2Mo$ (599.55) C: 50.08, H: 5.04, N: 2.34. Found C: 50.15, H: 5.20, N: 2.14.

3. Results and discussion

3.1. Synthesis of the anionic complex $[Et_4N][Mo(CO)_5(PPh_2CS_2)]$ (3)

Abstraction of a proton from the metal coordinated phosphine has been reported for the synthesis of the phosphorus derivatives [4]. Interestingly, up to now, only a few examples are known for dialkylphosphinodithioformato ligand, $R_2PCS_2^-$. These $R_2PCS_2^-$ ligands are probably air-sensitive and oxidized easily to give $R_2P(X)CS_2$ (X = O, S).



Scheme 1.

Complex $[Et_4N][Mo(CO)_5(PPh_2)]$ (**1**) was produced in high yield by the reaction of $Mo(CO)_5(HPPh_2)$ with *n*-BuLi in diethyl ether ($-78°C$) in the presence of Et_4NBr. The slightly air-sensitive yellow compound **1** is soluble in CH_2Cl_2 and CH_3CN and insoluble in *n*-hexane and diethyl ether. The ^{13}C-NMR of **1** reveals two resonances at δ 205.7 and 210.0 with a 4:1 ratio, which are assigned to the carbon atoms of the *cis* and *trans* carbonyl groups, respectively. Complex $[Et_4N][Mo(CO)_5(PPh_2CS_2)]$ (**3**) can be obtained by two routes (Scheme 1). Both treatment of **1** with CS_2 and the reaction of $Mo(CO)_5(CH_3CN)$ with $[Et_4N][PPh_2CS_2]$ (**2**) lead to the formation of **3** in 87 and 84% yield, respectively. The red complex **3** is stable in solid-state and undergoes decarbonylation reaction in solution (described below). The analytical data of **3** are in agreement with the formula. FAB mass spectrum of **3** shows a base peak with a typical Mo isotope pattern corresponding to the $[M^+ + Et_4N]$ molecular mass. The IR spectrum of **3** shows three terminal carbonyl stretchings ($2A_1 + E$) that reveal a typical pattern for a $LM(CO)_5$ unit with an octahedral geometry. Down-field shift of the ^{31}P resonance of **3** (δ 69.8) relative to that of **1** indicates formation of the $Ph_2PCS_2^-$ ligand and transfer of electron density from the phosphorus atom to the CS_2 portion. The ^{13}C-NMR of **3** reveals three resonances at δ 204.8 ($J_{P-C} = 7.5$ Hz), 209.3 ($J_{P-C} = 25.5$ Hz) and 235.7 assignable to the carbon atoms of the *cis* carbonyl groups and the *trans* carbonyl group and the carbon disulfide, respectively.

Kunze, Ambrosius and co-workers [5] have synthesized the anionic heteroallyl ligands containing phosphorus such as $R_2P(X)C(Y)NR^-$ or $R_2PC(Y)NR^-$ (X = O or S, Y = O or S). Notably, all of these anionic heteroallyl ligands bound to transition metals through O and S [5a], N and S [5c,d], S and S [5e], P and S [5b,d, f–i] and no mono-dentate phosphorus coordination has been observed. Obviously, **3** is formed via abstraction of a proton by *n*-BuLi, followed by the addition of the resulting phosphido unit onto the carbon atom of CS_2. In 1987, Hey and co-workers reported the insertion reaction of CS_2 into a Zr–P [2] bond, forming the dialkylphosphinodithioformato ligand, $R_2PCS_2^-$. The bis(trimethylsily)phosphino zirconium complex $[Zr(\eta^5\text{-}C_5H_5)_2\{\eta^2\text{-}S_2CP(SiMe_3)_2\}Cl]$, obtained from the reaction of $[Zr(\eta^5\text{-}C_5H_5)_2(PR_2)X]X$ ($R = SiMe_3$, $X = Cl$ or Me) with CS_2, contains a $R_2PCS_2^-$ ligand chelating through the two sulfur atoms of the CS_2 moiety. No insertion of CS_2 into the metal–phosphine bond was observed for our tungsten- and molybdenum complexes. Instead, the dithiocarbamato ligand, $R_2NCS_2^-$ was synthesized by the insertion reac-

tion of CS_2 into the M–N bond (M = Cr, Mo, W) [6b]. The fact that the formation of **3** was observed in two different synthetic routes clearly indicates that **3** is a thermodynamic product and the P-coordination seems to be more favorable than the S-coordination for the $Ph_2PCS_2^-$ ligand.

3.2. Alkylation and acylation of $[Et_4N][Mo(CO)_5(PPh_2CS_2)]$ (3)

To explore the reactivity of complex **3**, we carried out the reactions of **3** with several alkyl halides and acyl halide. The reaction of **3** with C_2H_5I in CH_2Cl_2 gave the neutral complex $Mo(CO)_5[PPh_2(CS_2C_2H_5)]$ (**4**). This red powder was isolated in 85% yield. Extraction with *n*-hexane followed by removal of the solvent gave the analytically pure product **4**. Complex **4** is stable in refluxing CH_3CN or C_6H_6 under N_2. The FAB mass spectrum of **4** shows a base peak in agreement with the $[M^+]$ ion fragment. The ^{1}H-NMR spectrum of **4** exhibits two resonances at δ 1.32 and 3.29 with a 3:2 ratio attributed to the ethyl protons and the corresponding resonances in the ^{13}C-NMR spectrum appear at δ 11.8 and 32.0, respectively. The ^{31}P-NMR spectrum of **4** shows a resonance at δ 75.6, close to that of **3**. On the basis of these spectroscopic data, it is likely that the alkylation takes place at one of the sulfur atom. This result is consistent with that of the analogue complex $W(CO)_5[PPh_2(CS_2Me)]$ [3c], which was structurally confirmed by an X-ray diffraction analysis. The other alkylated complexes $Mo(CO)_5[PPh_2(CS_2R)]$ (R = C_2H_4OH, **5**; C_3H_5; **6**) have been prepared in a similar way. In the mass spectra of **5** and **6**, the molecular ion along with the $[M^+ - CO]$ peak are detected. The ^{13}C-NMR spectra of **5** and **6** both reveal singlet resonances at δ 39.9 and 59.9 for **5** and δ 41.5, 120.5 and 129.6 for **6**, which are assigned to the carbon atoms of the SCH_2CH_2OH and $SCH_2CH{=}CH_2$ groups, respectively. By comparing the spectroscopic data of the alkylated molybdenum complexes with that of the corresponding alkylated tungsten complexes [3e], it is clear that the organic segments have the same chemical environment, namely, *S*-alkylation.

In the reaction of **3** with 1-naphthoyl chloride $[C_{10}H_7C(O)Cl]$, complex **7** was obtained. The lower yield of this green complex relative to the higher yields of the alkylation products may result from its air- and moisture-sensitive character. The IR absorption of the acyl group of **7** appears at 1726 cm^{-1} and the ^{13}C-NMR resonance at δ 170.0. Interestingly, chemical shifts of the ^{31}P resonances of all the alkylated and acylated complexes all fall within the region of δ 75–78, indicating similar structure for all these complexes. Although the differences are small, ^{31}P chemical shift moves toward down-field region as the group attached to the phosphine ligand becoming more electron-withdrawing.

This alkylation reaction was extended for CH_2I_2 in order to synthesize dinuclear complex. The reaction of **3** with excess CH_2I_2 in CH_2Cl_2 gave the dinuclear complex $[Mo(CO)_5(PPh_2CS_2)]_2(\mu\text{-}CH_2)$ (**8**). The proposed monomeric complex $Mo(CO)_5[PPh_2(CS_2CH_2I)]$ was not detected in the reaction. The ^{1}H-NMR spectrum of **8** exhibits a resonance at δ 4.99 assignable to the CH_2 group and the corresponding ^{13}C-NMR signal is at δ 42.4. The ^{31}P-NMR spectrum of **8** shows a resonance at δ 77.0. The FAB mass spectrum of **8** shows a base peak at m/z 730 corresponding to $[Mo(PPh_2CS_2)]_2(\mu\text{-}CH_2)$, formed by loss of ten CO groups from **8** and this phenomenon was also observed for the complex $[W(Co)_5(PPh_2CS_2)]_2(\mu\text{-}CH_2)$ [3e]. On the basis of these data, it is clear that the two metal centers are connected by the $(Ph_2PCS_2)_2CH_2$ bridge.

3.3. Decarbonylation of $[Et_4N][Mo(CO)_5(PPh_2CS_2)]$ (3)

When the CH_3CN solution of **3** was stirred, decarbonylation occurred affording a stable compound which can be formulated as $[Et_4N][Mo(CO)_4(PPh_2CS_2)]$ (**9**) based on its analytical and spectroscopic data (Scheme 1). The IR spectrum of **9** shows a pattern different from that of $M(CO)_5L$. The four IR absorptions at 2009, 1893, 1865, 1827 cm^{-1}, are typical for a $M(CO)_4$ [6] unit with a pseudooctahedral geometry. The ^{31}P-NMR spectrum of **9** shows a resonance at δ 38.9. The significant up-field shift of the ^{31}P resonance of **9** relative to that of **3** (δ 69.8) suggests a distinctively different chemical and electronic environment for the $R_2PCS_2^-$ ligand which supports its structure depicted in Scheme 1. Kunze and Cotton have reported complexes with similar coordination via the P and S atoms in the hetero-allylic Ph_2PCSNR^- ligands [5]. Notably, the decarbonylation reaction of **3** occurred in acetonitrile instantly but very slowly in dichloromethane. The phenomenon probably caused by better donor ability of CH_3CN than CH_2Cl_2. The acylation and alkylation reaction of **3** can also be carried out in CH_2Cl_2 and the alkylated products can be obtained in higher yield.

4. Concluding remarks

This study describes the chemical behavior of the anionic diphenylphosphinodithioformato Mo(0) complex $[Et_4N][Mo(CO)_5(PPh_2CS_2)]$ (**3**) toward alkylation, acylation and decarbonylation reactions. By comparing with our previous study of the W analogues, significant differences between the Mo and W complexes in solubility, stability and nucleophilicity are observed. Notably, the decarbonylation reaction is spontaneous for Mo but requires heating for the W complex. The molybdenum complexes with the $Ph_2PCS_2^-$ ligand are more soluble in common organic solvents than the corresponding tung-

sten complexes but the stability of molybdenum complexes are lower and with weaker nucleophilicity.

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