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Reactivity studies of η^2-acyl complexes of molybdenum: reactions with strong bases and with bidentate phosphines☆

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Abstract

New η^2-isopropyl–acyl complexes of formula $Mo(\eta^2\text{-}C(O)CHMe_2)(L)(CO)(PMe_3)_2$ ($L = S_2CNC_4H_4$, $H_2B(pz)_2$; pz = 1-pyrazolyl) have been prepared from the reaction of an excess of KH with $Mo(\eta^2\text{-}C(O)CH_3)(L)(CO)(PMe_3)_2$ and subsequent addition of an excess of MeI. At ambient temperature, solutions of the isopropyl–acyl derivatives gradually evolve to the hydrides $MoH(L)(CO)_2(PMe_3)_2$ and propene. The η^2-acyls $Mo(\eta^2\text{-}C(O)Me)(L)(CO)(PMe_3)_2$ complexes ($L = H_2B(pz)_2$, Bp; $H_2B(3,5\text{-}Me_2pz)_2$, Bp^{Me_2}) as well as the related derivatives of dithioacid ligands, $Mo(C(O)Me)(L)(CO)(PMe_3)_2$ ($L = Me_2NCS_2$, *i*-$PrOCS_2$) react with the chelating phosphines $R_2PCH_2CH_2PR_2$ (R = Me, dmpe; Et, depe) with replacement of the two PMe_3 by the bidentate diphosphine. A similar substitution is observed in the reaction of $Mo(\eta^2\text{-}C(O)Me)Cl(CO)(PMe_3)_3$ with depe, whereas in this case dmpe gives a mixture of $Mo(\eta^2\text{-}C(O)Me)Cl(CO)(dmpe)(PMe_3)$ and the cationic complex $[Mo(\eta^2\text{-}C(O)Me)(CO)(dmpe)_2]Cl$.

Keywords: Molybdenum; Acyl complexes; Enolates; Reactivity; Diphosphines

1. Introduction

The acyl ligand is an important organometallic functionality which has been the subject of many reactivity studies [1]. Metal-bound enolate complexes have attracted attention because of their utility as asymmetric induction reagents in many areas of organic and organometallic chemistry [2,3]. It is well known from the literature that powerful deprotonating reagents such as Li*n*-Bu, KH, $LiN(CHMe_2)_2$ or $LiN(SiMe_3)_2$ can be used for the preparation of enolate species by reaction with transition metal acyl complexes. η^1 and η^2 coordination modes of acyl ligands exhibit this type of reactivity and a relatively large number of enolate derivatives have been synthesized by using this procedure. In subsequent reactions with alkyl halides the enolates can be alkylated at the C_β, leading to complexes containing an elaborated acyl group [4]. We were interested in determining if the acyl complexes $Mo(\eta^2\text{-}C(O)CH_3)(L)(CO)(PMe_3)_2$ [5,6] (L = monoanionic bidentate ligand), for which the alkyl (carbonyl) structure $Mo(CH_3)(L)(CO)_2(PMe_3)_2$ appears to be readily accessible, can undergo a similar reactivity. In this paper we report the results of the studies of the reactions of these Mo–acyl complexes with strong bases and posterior addition of alkyl halides. The outcome of the reactions of various η^2-acyls of Mo with bidentate phosphines is also described.

☆ Dedicated to Professor Alan Cowley on his 65th birthday.

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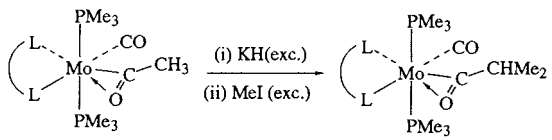
2. Results and discussion

2.1. Sequential reaction of [Mo](η^2-C(O)Me) complexes with KH and MeI. Synthesis of the compounds Mo(η^2-C(O)-i-Pr)(L)(CO)(PMe_3)$_2$ (L = dihydrobis(1-pyrazolyl)borate, Bp, **1a**; $S_2CNC_4H_4$, **1b**)

Treatment of a purple solution of the pyrrol-derived dithiocarbamate–acetyl complex Mo(η^2-C(O)Me)($S_2CNC_4H_4$)(CO)(PMe_3)$_2$, with an excess of KH at 0°C, instantly produces a blue suspension. Subsequent addition at the same temperature of a large excess of MeI restores the purple colour and from the resulting mixture purple crystals of the new complex Mo(η^2-C(O)-*i*-Pr)($S_2CNC_4H_4$)(CO)(PMe_3)$_2$ (**1b**), can be isolated in ca. 50% yield (Eq. (1)).



L-L = Bp (**1a**)
$S_2CNC_4H_4$ (**1b**) (1)

In order to avoid decomposition of this complex, the work-up should be effected at temperatures close to, or preferably below, 0°C. Starting with the related dihydrobis(1-pyrazolyl)borate complex, the corresponding isopropyl-derived η^2-acyl compound **1a** can be obtained as red crystals in 70% yield. In this case, however, the purported enolate intermediate (vide infra) has a bright yellow colour (as opposed to blue, in the reaction leading to **1b**). Further elaboration of the acyl ligand to give a –C(O)-*t*-Bu derivative, as observed by Templeton and co-workers for the related Mo(η^2-C(O)Me)L(CO)(L′) complexes [4b] (L = hydrotris(1-pyrazolyl)borate ligand, L′ = CO, $P(OR)_3$) has proved unsuccessful. The use of longer reaction times and of a large excess of KH and MeI yields only decomposition products.

The new acyls **1a** and **1b** have been characterized by elemental analysis and by spectroscopic methods (IR; ^{1}H-, ^{13}C- and ^{31}P-NMR). In accord with the proposed formulation, their IR spectra exhibit bands in the proximity of 1780 and 1500 cm^{-1}, due to the terminal carbonyl and η^2-acyl ligands, respectively, (e.g. 1775 and 1500 cm^{-1}, data for **1a**). These functionalities are responsible for the appearance of ^{13}C{^{1}H}-NMR resonances in the proximity of 240 (Mo–CO) and 280 ppm (Mo–C(O)R). For example, in the case of **1a** these signals have chemical shifts of 238.6 and 278.7 ppm, respectively, and appear as triplets due to coupling to two equivalent ^{31}P nuclei (see Section 3). In this regard it should be finally noted that compounds **1** display a fluxional behaviour in solution which is associated with a librational motion of the acyl ligand [7]. Thus, at −30°C the two ^{31}P nuclei of **1b** appear equivalent and give rise to a singlet at δ 12.1, whilst at −90°C they originate an AB spin pattern, characterized by δ_A = 10.7, δ_B = 15.3 and $^2J_{AB}$ = 74 Hz. This coupling is clearly indicative of a *trans* distribution of the PMe_3 groups.

As already indicated, complexes **1** are unstable in solution at temperatures above 0°C. To understand their chemical behaviour under ambient conditions the evolution of the bis(pyrazolyl)borate derivative **1a** has been monitored at 20°C by NMR spectroscopy. A C_6D_6 solution of this compound, when maintained in an NMR tube for 24 h, leads cleanly to propene plus a hydride species. This has been identified as Mo-H(Bp)(CO)$_2$(PMe_3)$_2$ by comparison of its NMR parameters with those reported for other related MoH(L)(CO)$_2$(PMe_3)$_2$ derivatives [8] (L represents a monoanionic, bidentate S- or O-donor ligand). Thus the Mo–H unit gives rise to a high-field triplet at δ −4.17 ($^2J_{HP}$ = 37 Hz) and the two carbonyl groups appear also as a low-field triplet in the ^{13}C{^{1}H}-NMR spectrum (δ 223, $^2J_{CP}$ = 15 Hz). No intermediates have been detected in the reaction pathway leading to this hydride compound. Nevertheless the nature of the final products and the chemical reactivity known for other related η^2-acyl complexes [6,9] suggest that the decomposition reaction involves CO deinsertion to give a transient seven-coordinate alkyl intermediate which then undergoes a β-H elimination reaction with posterior dissociation of the resulting olefin (the vacant coordination site needed for the latter process could be created by the temporary dissociation of one of the pyrazolyl rings of the Bp ligand or one of the phosphine ligands).

In an attempt to gain information on the deprotonation of the η^2-acyls Mo(η^2-C(O)Me)(L)(CO)(PMe_3)$_2$ (L = Bp, $S_2CNC_4H_4$), other strong bases like Li*n*-Bu and KN($SiMe_3$)$_2$ have been used. Intermediate species similar to those formed in the reaction with KH were detected but no clean products were isolated following the addition of MeI. Also the reactions of the agostic acetyls Mo(C(O)Me)(L)(CO)(PMe_3)$_2$ (L = S_2CNMe_2, S_2CN-*i*-Pr_2) and of the dihaptoacetyls Mo(η^2-C(O)Me)(L)(CO)$_2$(PMe_3) (L = S_2CNMe_2, acac) with the above deprotonating reagents, followed by addition of MeI were studied. The expected acyls could not be isolated, only the hydride MoH(S_2CNMe_2)(CO)$_2$-(PMe_3)$_2$ was identified among the products of the reaction involving the S_2CNMe_2 derivative containing the agostic acyl ligand. It seems likely that the deprotonation reaction gives the expected enolates, e.g. [Mo(C(O) = CH_2)(L)(CO)(PMe_3)$_2$]$^-$ and that these subsequently undergo alkylation by MeI. Unfortunately their high reactivity under our experimental conditions has prevented their isolation and

characterization. A complex containing an η^2-$C(O)CH_2Me$ ligand is also expected as an intermediate in the reaction leading to complexes **1** but, once again, and despite our efforts, no conclusive evidence about its formation has been gained during the progress of this work.

2.2. Reactions of [Mo](η^2-C(O)Me) complexes with $R_2PCH_2CH_2PR_2$ (R = Me, Et)

The interaction of the η^2-acyls $Mo(\eta^2$-$C(O)Me)(L)(CO)(PMe_3)_2$ [6] (L = Bp; dihydrobis(3,5-dimethylpyrazolyl)borate, Bp^{Me_2}) with Me_2PCH_2-CH_2PMe_2 (dmpe) occurs with substitution of the monodentate phosphines by the chelating dmpe, without altering the Mo-η^2-acyl linkage (Eq. (2)).

$$Mo(\eta^2\text{-}C(O)Me(L)(CO)(PMe_3)_2 \xrightarrow[-2\ PMe_3]{dmpe} Mo(\eta^2\text{-}C(O)Me)(L)(CO)(dmpe) \quad (2)$$

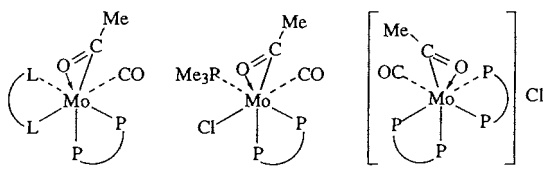
where L = Bp, **2a**; Bp^{Me_2}, **2b**.

Interestingly, during the course of the analogous reaction of the agostic acetyls Mo(C(O)Me)(L)(CO)$PMe_3)_2$ (L = S_2CNMe_2, S_2CO-*i*-Pr) [5], the acyl moiety becomes dihaptobonded to Mo. This clearly confirms the subtle nature of the steric and electronic factors that stabilize the Mo-agostic acyl interaction (Eq. (3)).

$$Mo(C(O)Me)(L)(CO)(PMe_3)_2 \xrightarrow[-2\ PMe_3]{dmpe} Mo(\eta^2\text{-}C(O)Me)(L)(CO)(dmpe) \quad (3)$$

where L = S_2CNMe_2, **2c**; S_2CO-*i*-Pr, **2d**.

The transformations summarized in Eqs. (2) and (3) proceed cleanly and provide high yields of compounds **2**. An excess of dmpe has no deleterious effect. The acyl group in compounds **2** has spectroscopic properties similar to those found in other analogous acyl complexes, thereby the proposed dihapto coordination. The following spectroscopic evidence, and other data summarized in Section 3 are in favour of structure **A** for these complexes: (i) the observation of AB spin systems in the $^{31}P\{^1H\}$-NMR spectra (e.g. $\delta_A = 40.1$; $\delta_B = 47.8$; $^2J_{AB} = 28$ Hz, data for **2a**) and (ii) the non equivalence of the pz rings of complexes **2a** and **2b** detected in the ^1H- and $^{13}C\{^1H\}$-NMR spectra.



Treatment of THF solutions of the chloro–methyl complex $Mo(\eta^2$-$C(O)Me)Cl(CO)(PMe_3)_3$ [5c] with depe ($Et_2PCH_2CH_2PEt_2$) results in the rapid displacement of two molecules of PMe_3 and formation of the expected product $Mo(\eta^2$-C(O)Me)Cl(CO)(depe)(PMe_3) (**3**), as shown in Eq. (4):

$$Mo(\eta^2\text{-}C(O)Me)Cl(CO)(PMe_3)_3 \xrightarrow{depe} \underset{\mathbf{3}}{Mo(\eta^2\text{-}C(O)Me)Cl(CO)(depe)(PMe_3)} \quad (4)$$

Probably due to steric reasons, only one molecule of the diphosphine becomes incorporated to the coordination sphere of the metal, even in the presence of an excess of the reagent and under rather forcing conditions (50°C, 24 h). This contrast with the similar reaction involving the smaller dmpe which affords a mixture of the mono and bis(dmpe) complexes $Mo(\eta^2$-C(O)Me)Cl(CO)(dmpe)(PMe_3) (**4**), and [$Mo(\eta^2$-C(O)Me)(CO)$(dmpe)_2$]Cl (**5**), respectively. Monitoring of the progress of the reaction by $^{31}P\{^1H\}$-NMR spectroscopy reveals the initial formation of **4** followed by its fast conversion into **5** if sufficient dmpe is available.

At variance with complex **3**, which is an orange crystalline material, compounds **4** and **5** cannot be isolated in analytically pure form, crystallized solids being always contaminated with small amounts of the starting material and of other products resulting from their ready decomposition. The bis(dmpe) derivative **5** is particularly unstable in solution and decomposes to a mixture of the known cationic species [Mo-$H(CO)_2(dmpe)_2]^+$ [10] and $[MoOCl(dmpe)_2]^+$ [11]. It is likely that adventitious water (and perhaps O_2) plays an important role in this transformation, but we have not investigated this decomposition any further.

The $^{31}P\{^1H\}$-NMR spectra of compounds **3** and **4** consist of essentially first order AMX spin systems. The unique PMe_3 ligand is strongly coupled to one of the ^{31}P nuclei of the diphosphine ($^2J_{PP} = 165$–170 Hz) and therefore the three P atoms adopt a meridional distribution. Since only small couplings of 23 and 7 Hz are detected for the terminal carbonyl ligand, a structure having a *trans*-P–Mo–CO arrangement can be ruled out. By similarity with the structure found for other related η^2-acyls, geometry **B** is favoured for these complexes, although an alternative proposal having *trans* CO and acyl ligands cannot be discounted with the spectroscopic data available. As for **5**, the existence of an AMQX spin system in the $^{31}P\{^1H\}$-NMR spectrum, in addition to other data (e.g. ^{13}C–^{31}P coupling of 50 and 16 Hz for the CO ligand) are in accord with formulation C.

3. Experimental

3.1. General

Microanalyses were carried out by Pascher Microanalytical Laboratories, Remagen, Germany, and the Analytical Service of the University of Sevilla. IR spectra

were recorded as Nujol mulls or in an appropriate solvent on Perkin–Elmer model 684 spectrometer. The ^{1}H-, ^{13}C- and ^{31}P-NMR spectra were run on a Varian XL-200 or on Bruker AMX-300 or AMX-500 instruments. ^{1}H-NMR shifts were referenced to the residual signals of the deuterated solvent employed, while $^{13}C\{^{1}H\}$ resonances were correlated with the characteristic signal of the solvent. $^{31}P\{^{1}H\}$-NMR shifts were referenced to external 85% phosphoric acid. All data are reported in ppm downfield from $SiMe_4$.

All preparations and manipulations were carried out under oxygen-free nitrogen or argon, following conventional Schlenk techniques. Solvents were dried and degassed before use. All reagents were either purchased from commercial suppliers or prepared according to published procedures.

3.2. Preparations

3.2.1. Preparation of $Mo(\eta^2\text{-}C(O)CHMe_2)(L)(CO)(PMe_3)_2$, ($L = Bp$, **1a**, $S_2CNC_4H_4$, **1b**)

In a representative synthesis, a solution of $Mo(\eta^2\text{-}C(O)Me)Bp(CO)(PMe_3)_2$ (0.47 g, 1.0 mmol) in 30 ml of THF at 0°C was slowly transferred by cannula into a flask containing an excess of KH (0.12 g, 3.0 mmol, prepared from commercial 35% dispersion in mineral oil) in 30 ml of THF. The colour of the solution changed instantaneously from red to gold–yellow. After stirring at 0°C for ca. 20 min, an excess of MeI (0.5 ml, ca. 8 mmol) was slowly added. The stirring was continued for 20 min at 0°C whereupon the resulting suspension took the original red colour of the starting dihapto-acyl. The solvent was evaporated from this suspension in vacuo and the residue extracted at 0°C with 25 ml of petroleum ether. Centrifugation and cooling at −35°C afforded $Mo(\eta^2\text{-}C(O)CHMe_2)(Bp)(CO)(PMe_3)_2$ as red crystals in 70% yield. Anal. Calc. C 41.3, H 7.3, N 11.3; Found: C 41.4, H 6.7, N 11.3. IR (Nujol mull, cm^{-1}): ν(CO) 1776 (s), 1501 (m). ^{1}H-NMR (C_6D_6): δ 0.95 (pseudo t, $J_{HPapp} = 3.5$ Hz, 2 $P(CH_3)_3$), 1.05 (d, $J_{HH} = 6.9$ Hz, $CH(CH_3)_2$), 3.87 (h, $J_{HH} = 6.9$ Hz, $CH(CH_3)_2$), 5.93 (t, $J_{HH} = 2.1$ Hz, CH, Bp), 5.96 (t, $J_{HH} = 2.1$ Hz, CH, Bp), 7.25, 7.58, 7.60, 7.75 (brs, 4 CH, Bp). $^{13}C\{^{1}H\}$-NMR (THF/CD_3COCD_3, −5°C): δ 16.0 (pseudo t, $J_{CPapp} = 10$ Hz, 2 $P(CH_3)_3$), 17.7 (s, $CH(CH_3)_2$), 39.3 (s, $CH(CH_3)_2$), 103.8, 105.2, 135.6, 136.9, 137.5, 146.9 (s, 6 CH, Bp), 238.6 (t, $J_{CP} = 13$ Hz, CO), 278.7 (t, $J_{CP} = 19$ Hz, $C(O)CH(CH_3)_2$). $^{31}P\{^{1}H\}$-NMR (C_6D_6): δ 3.4 (brs).

Temperatures below 0°C were also kept during the preparation of the complex $Mo(\eta^2\text{-}C(O)CHMe_2)(S_2CNC_4H_4)(CO)(PMe_3)_2$, which was obtained (from $Mo(\eta^2\text{-}COMe)(S_2CNC_4H_4)(CO)(PMe_3)_2$) by a similar procedure as purple red crystals in ca. 50% yield. Anal. Calc. C 39.3, H 5.9, N 2.9; Found: C 38.7, H 5.9, N 2.7. IR (Nujol mull, cm^{-1}): ν(CO) 1777 (s), 1519 (m). ^{1}H-NMR ($C_6D_5CD_3$): δ 1.06 (d, $J_{HH} = 6.9$ Hz, $CH(CH_3)_2$), 1.37 (pseudo t, $J_{HPapp} = 3.5$ Hz, 2 $P(CH_3)_3$), 3.66 (h, $J_{HH} = 6.9$ Hz, $CH(CH_3)_2$), 6.11 (pseudo t, $J_{HHapp} = 2.2$ Hz, 2 CH, pyrrol), 7.86 (pseudo t, $J_{HHapp} = 2.2$ Hz, 2 CH, pyrrol). $^{13}C\{^{1}H\}$-NMR (THF/CD_3COCD_3): δ 15.2 (pseudo t, $J_{CPapp} = 12$ Hz, 2 $P(CH_3)_3$), 17.8 (s, $CH(CH_3)_2$), 41.5 (s, $CH(CH_3)_2$), 112.3, 117.3 (s, 4 CH, pyrrol), 237.6 (t, $J_{CP} = 16$ Hz, CO), 285.1 (t, $J_{CP} = 15$ Hz, $C(O)CH(CH_3)_2$). $^{31}P\{^{1}H\}$-NMR (CD_3COCD_3, −30°C): δ 12.1 (s). $^{31}P\{^{1}H\}$-NMR (CD_3COCD_3, −90°C): δ 10.7 (d, $J_{PP} = 74$ Hz), 15.3 (d, $J_{PP} = 74$ Hz).

3.2.2. Spectroscopic characterization of $Mo(H)(Bp)(CO)_2(PMe_3)_2$

^{1}H-NMR (C_6D_6): δ −4.71 (t, $J_{HP} = 37$ Hz, MoH), 0.76 (pseudo t, $J_{HPapp} = 3.3$ Hz, 2 $P(CH_3)_3$), 5.93 (t, $J_{HH} = 3.4$ Hz, 2 CH, Bp), 7.57, 7.60 (brs, 4 CH, Bp). $^{13}C\{^{1}H\}$-NMR (C_6D_6): δ 16.6 (pseudo t, $J_{CPapp} = 12$ Hz, 2 $P(CH_3)_3$), 104.8, 136.6, 144.3 (s, 6 CH, Bp), 223.8 (t, $J_{CP} = 15$ Hz, CO). $^{31}P\{^{1}H\}$-NMR (C_6D_6) δ −2.8 (s).

3.2.3. $Mo(\eta^2\text{-}C(O)CH_3)(L)(CO)(dmpe)$ $L = Bp$, **2a**; Bp^{Me_2}, **2b**

1,2-Bis(dimethylphosphino)ethane (dmpe; 0.1 ml, ca. 0.5 mmol) was added to a red solution of $Mo(\eta^2\text{-}C(O)CH_3)(Bp)(CO)(PMe_3)_2$ (0.46 g, 0.5 mmol) in 50 ml of THF. The resulting solution was stirred at room temperature (r.t.) for 1 h, the solvent was evaporated under reduced pressure, and the residue extracted with acetone. After centrifugation, partial evaporation of the solvent and cooling at 5°C, $Mo(\eta^2\text{-}C(O)CH_3)(Bp)(CO)$-(dmpe) was obtained as yellow–orange crystals in 50% yield. Anal. Calc. C 38.7, H 5.8, N 12.1; Found: C 38.0, H 5.6, N 11.7. IR (Nujol mull, cm^{-1}): ν(CO) 1779 (s), 1551 (m). ^{1}H-NMR (C_6D_6): δ 0.88 (d, $J_{HP} = 7.9$ Hz, PCH_3), 1.09 (d, $J_{HP} = 8.9$ Hz, PCH_3), 1.13 (d, $J_{HP} = 7.4$ Hz, PCH_3), 1.48 (d, $J_{HP} = 8.1$ Hz, PCH_3), 1.60 (brs, 2 PCH_2), 2.28 (s, $C(O)CH_3$), 5.90 (t, $J_{HH} = 2.1$ Hz, CH), 6.12 (t, $J_{HH} = 2.0$ Hz, CH), 6.73 (d, $J_{HH} = 2.0$ Hz, CH), 7.62 (t, $J_{HH} = 2.3$ Hz, CH), 7.75 (d, $J_{HH} = 2.0$ Hz, CH), 8.36 (d, $J_{HH} = 1.9$ Hz, CH). $^{13}C\{^{1}H\}$-NMR (C_6D_6): δ 14.3 (d, $J_{CP} = 26$ Hz, PCH_3), 15.5 (d, $J_{CP} = 15$ Hz, PCH_3), 19.0 (d, $J_{CP} = 17$ Hz, PCH_3), 20.0 (d, $J_{CP} = 31$ Hz, PCH_3), 30.1 (m, 2 PCH_2), 30.1 (s, $C(O)CH_3$), 104.2, 105.3, 135.3, 137.4, 143.7, 147.3 (s, 6 CH, Bp), CO and $C(O)R$ resonances not detected due to solubility problems. $^{31}P\{^{1}H\}$-NMR (C_6D_6): δ 40.1, 47.8 (d, $J_{PP} = 28$ Hz).

Using $Mo(\eta^2\text{-}C(O)CH_3)(Bp^{Me_2})(CO)(PMe_3)_2$ as the starting material, $Mo(\eta^2\text{-}C(O)CH_3)(Bp^{Me_2})(CO)$(dmpe) (**2b**) was obtained by the same method in similar yields. Anal. Calc. C 43.8, H 6.7, N 10.8; Found: C 43.4, H 6.5, N 11.1. IR (Nujol mull, cm^{-1}): ν(CO) 1798 (s),

1515 (w). ^{1}H-NMR (CD_2Cl_2): δ 1.32 (d, $J_{HP} = 7.4$ Hz, PCH_3), 1.47 (d, $J_{HP} = 9.1$ Hz, PCH_3), 1.48 (d, $J_{HP} = 7.4$ Hz, PCH_3), 1.88 (d, $J_{HP} = 7.6$ Hz, PCH_3), 1.93, 2.22, 2.25, 2.32 (s, 4 CH_3, Bp^{Me_2}), 2.01 (brs, 2 PCH_2), 3.00 (s, C(O)CH_3), 5.67, 5.86 (s, 2 CH, Bp^{Me_2}). ^{13}C{^{1}H}-NMR (CD_2Cl_2): δ 13.1, 13.1, 15.1, 15.8 (s, 4 CH_3, Bp^{Me_2}), 15.2 (d, $J_{CP} = 28$ Hz, PCH_3), 16.0 (d, $J_{CP} = 29$ Hz, PCH_3), 18.4 (d, $J_{CP} = 15$ Hz, PCH_3), 20.9 (d, $J_{CP} = 18$ Hz, PCH_3), 29.0 (dd, $J_{CP} = 34$, 14 Hz, PCH_2), 31.3 (s, C(O)CH_3), 31.7 (dd, $J_{CP} = 29$, 15 Hz, PCH_2), 105.6, 106.5 (s, 2 CH, Bp^{Me_2}), 143.6, 144.2, 148.1, 152.2 (s, 4 CCH_3, Bp^{Me_2}), 232.4 (dd, $J_{CP} = 26$, 10 Hz, CO), 270.1 (dd, $J_{CP} = 27$, 12 Hz, C(O)CH_3). ^{31}P{^{1}H}-NMR (CD_2Cl_2): δ 42.6, 48.0 (d, $J_{PP} = 13$ Hz).

3.2.4. Preparation of $Mo(\eta^2\text{-}C(O)CH_3)(L)(CO)(dmpe)$. $L = Me_2NCS_2$, **2c**; $i\text{-}PrOCS_2$, **2d**

To a stirred, red solution of $Mo(C(O)CH_3)(S_2CNMe_2)(CO)(PMe_3)_2$ (0.45 g, 1.0 mmol) in 30 ml of Et_2O was added dmpe (0.2 ml, ca. 1 mmol). The desired complex crystallized directly from the reaction mixture over a period of a few minutes after the addition of dmpe. The mixture was stirred for 1 h to ensure completion of the reaction. This suspension was evaporated to dryness and the residue extracted with a 1:1 mixture of petroleum ether and dichloromethane. Further centrifugation and slow evaporation of the solvent produced the expected product as red crystals in 60% yield. Anal. Calc. C 33.0, H 5.7, N 3.2; Found: C 33.0, H 5.7, N 3.3. IR (Nujol mull, cm^{-1}): ν(CO) 1768 (s), 1460 (w); ν(CN) 1515 (m). ^{1}H-NMR (C_6D_6): δ 1.12 (d, $J_{HP} = 8.2$ Hz, PCH_3), 1.25 (d, $J_{HP} = 8.2$ Hz, PCH_3), 1.35 (d, $J_{HP} = 8.2$ Hz, PCH_3), 1.4 (brs, 2 PCH_2), 1.66 (d, $J_{HP} = 8.2$ Hz, PCH_3), 2.50 (s, C(O)CH_3), 2.67, 2.76 (s, N$(CH_3)_2$). ^{13}C{^{1}H}-NMR (C_6D_6): δ 13.4 (d, $J_{CP} =$ 17 Hz, PCH_3), 15.7 (d, $J_{CP} = 31$ Hz, PCH_3), 19.0 (d, $J_{CP} = 24$ Hz, PCH_3), 19.3 (d, $J_{CP} = 24$ Hz, PCH_3), 27.9 (dd, $J_{CP} = 29$, 18 Hz, PCH_2), 29.9 (s, C(O)CH_3), 31.9 (dd, $J_{CP} = 28$, 21 Hz, PCH_2), 39.7, 40.7 (s, N$(CH_3)_2$), 214.3 (s, S_2C), 231.8 (dd, $J_{CP} = 14$, 7 Hz, CO), 274.4 (dd, $J_{CP} = 32$, 9 Hz, C(O)CH_3). ^{31}P{^{1}H}-NMR (C_6D_6): δ 50.7, 57.7 (d, $J_{PP} = 33$ Hz).

$Mo(\eta^2\text{-}C(O)CH_3)(S_2CO\text{-}i\text{-}Pr)(CO)(dmpe)$ (**2d**) was prepared by a route similar to that described above for **2c**, starting with $Mo(C(O)CH_3)(S_2CO\text{-}i\text{-}Pr)(CO)(PMe_3)_2$. It was isolated as red crystals in 90% yield. Anal. Calc. C 34.5, H 5.7; Found: C 34.5, H 6.1. IR (Nujol mull, cm^{-1}): ν(CO) 1789 (s), 1523 (w). ^{1}H-NMR (CD_3COCD_3): δ 1.32, 1.34 (d, $J_{HH} = 6.3$ Hz, $CH(CH_3)_2$), 1.33 (d, $J_{HP} = 8.3$ Hz, PCH_3), 1.4 (brs, 2 PCH_2), 1.64 (d, $J_{HP} = 8.3$ Hz, PCH_3), 1.68 (d, $J_{HP} = 9.0$ Hz, PCH_3), 1.86 (d, $J_{HP} = 8.5$ Hz, PCH_3), 2.90 (s, C(O)CH_3), 5.46 (h, $J_{HH} = 6.3$ Hz, $CH(CH_3)_2$). ^{13}C{^{1}H}-NMR (CD_3COCD_3): δ 13.3 (d, $J_{CP} = 16$ Hz, PCH_3), 15.8 (d, $J_{CP} = 31$ Hz, PCH_3), 19.5 (d, $J_{CP} = 25$ Hz, PCH_3), 20.0 (d, $J_{CP} = 25$ Hz, PCH_3), 28.3 (dd, $J_{CP} = 30$, 17 Hz, PCH_2), 29.6 (s, C(O)CH_3), 32.0 (dd, $J_{CP} = 29$, 21 Hz, PCH_2), 21.7, 21.7 (s, $CH(CH_3)_2$), 73.4 (s, $CH(CH_3)_2$), 232.4 (s, S_2C), 231.7 (dd, $J_{CP} = 12$, 9 Hz, CO), 274.1 (dd, $J_{CP} = 32$, 8 Hz, C(O)CH_3). ^{31}P{^{1}H}-NMR (CD_3COCD_3): δ 54.9, 62.2 (d, $J_{PP} = 33$ Hz).

3.2.5. Reaction of $Mo(\eta^2\text{-}C(O)CH_3)Cl(CO)(PMe_3)$ with depe. Preparation of $Mo(\eta^2\text{-}C(O)CH_3)Cl(CO)(depe)(PMe_3)$ (3)

To a red solution of $Mo(\eta^2\text{-}C(O)CH_3)Cl(CO)(PMe_3)_3$ (0.43 g, 1.0 mmol) in THF (50 ml), was added depe (0.23 ml, ca. 1 mmol) and the mixture was stirred at r.t. for 5 h. The solution remained red throughout. When the reaction was complete, the final solution was taken to dryness under reduced pressure, and the remaining residue was purified by crystallization from Et_2O (60–70 ml). This afforded $Mo(\eta^2\text{-}C(O)CH_3)Cl(CO)(depe)(PMe_3)$ (**3**), as orange crystals in 71% yield. Anal. Calc. C 39.6, H 7.4; Found: C 39.2, H 7.6. IR (Nujol mull, cm^{-1}) ν(CO): 1812 (s), 1520 (m). ^{1}H-NMR (CD_2Cl_2): δ 0.9 (brs, 4 PCH_2CH_3), 1.16 (d, $J_{HP} = 7.1$ Hz, $P(CH_3)_3$), 1.8 (brs, 6 PCH_2), 2.75 (s, C(O)CH_3). ^{13}C{^{1}H}-NMR (CD_2Cl_2): δ 7.8, 7.9, 8.2, 8.4 (s, 4 PCH_2CH_3), 14.0 (d, $J_{CP} = 20$ Hz, $P(CH_3)_3$), 17.3 (d, $J_{CP} = 15$ Hz, PCH_2CH_3), 18.4 (d, $J_{CP} = 20$ Hz, PCH_2CH_3), 19.0 (d, $J_{CP} = 29$ Hz, PCH_2CH_3), 20.7 (d, $J_{CP} = 19$ Hz, PCH_2CH_3), 22.2 (dd, $J_{CP} = 21$, 14 Hz, PCH_2CH_2), 23.2 (dd, $J_{CP} = 24$, 17 Hz, PCH_2CH_2), 31.3 (s, C(O)CH_3), 246.0 (ddd, $J_{CP} = 23$, 15, 7 Hz, CO), 272.9 (dt, $J_{CP} =$ 19, 10 Hz, C(O)CH_3). ^{31}P{^{1}H}-NMR (CD_2Cl_2): δ −5.4 (dd, $J_{PP} = 171$, 14 Hz, PMe_3), 62.3 (dd, $J_{PP} = 171$, 17 Hz, depe), 71.9 (dd, $J_{PP} = 17$, 14 Hz, depe).

3.2.6. Reaction of $Mo(\eta^2\text{-}C(O)CH_3)Cl(CO)(PMe_3)_3$ with dmpe. Characterization of $Mo(\eta^2\text{-}C(O)CH_3)Cl(CO)(dmpe)(PMe_3)$ (4) and $[Mo(\eta^2\text{-}C(O)CH_3)(CO)(dmpe)_2]Cl$ (5)

1,2-Bis(dimethylphosphine)ethane (0.4 ml, ca. 2 mmol) was added to a solution of $Mo(\eta^2\text{-}C(O)CH_3)Cl(CO)(PMe_3)_3$ (0.43 g, 1.0 mmol) in 50 ml of THF and the reaction mixture was stirred at r.t. overnight. The solvent was then evaporated to dryness and the residue washed twice with Et_2O and extracted with 20 ml of CH_2Cl_2. Concentration of this solution under reduced pressure and cooling at −35°C does not induce crystallization. However, the reaction product, **4e**, appears spectroscopically pure, since only a CO stretch at 1850 cm^{-1} and an AMQX pattern were evident in its IR and ^{31}P{^{1}H}-NMR (CH_2Cl_2 solution) spectra, respectively. Several solvent mixtures were attempted for the crystallization of this product with negative results. Further concentration under reduced pressure and addition of Et_2O (40 ml) yielded the orange cationic complex $[Mo(\eta^2\text{-}C(O)CH_3)(CO)(dmpe)_2]Cl$. This compound is extremely air-sensitive, and decomposes slowly even when kept under nitrogen, with formation of

$[MoH(CO)_2(dmpe)_2]Cl$ and $[MoOCl(dmpe)_2]Cl$ as the main decomposition products. Since complete separation of the latter impurities from $[Mo(\eta^2\text{-}C(O)CH_3)(CO)(dmpe)_2]Cl$ was difficult, satisfactory elemental analysis did not prove possible. Full characterization was however, accomplished by spectroscopic methods.

The mixing of equimolecular amounts of $Mo(\eta^2\text{-}C(O)CH_3)Cl(CO)(PMe_3)_3$ and dmpe in CH_2Cl_2 was monitored by $^{31}P\{^1H\}$-NMR spectroscopy. After 45 min of stirring at r.t. all the dmpe ligand had been consumed and a mixture of the starting material, $Mo(\eta^2\text{-}C(O)CH_3)Cl(CO)(dmpe)(PMe_3)$ and the bis-substituted product $[Mo(\eta^2\text{-}C(O)CH_3)(CO)(dmpe)_2]Cl$ could be observed. Addition of another equivalent of dmpe produced only the bis-dmpe complex after 3 h at r.t. in essentially quantitative yield (by $^{31}P\{^1H\}$-NMR spectroscopy). $Mo(\eta^2\text{-}C(O)CH_3)Cl(CO)(dmpe)(PMe_3)$ (**4**). IR (Nujol mull, cm^{-1}): ν(CO) 1820 (s), 1518 (m). ^1H-NMR (CD_2Cl_2): δ 1.25 (d, $J_{HP} = 7.2$ Hz, $P(CH_3)_3$), 1.38 (d, $J_{HP} = 7.2$ Hz, PCH_3), 1.40 (d, $J_{HP} = 8.0$ Hz, PCH_3), 1.4 (brs, 2 PCH_2), 1.45 (d, $J_{HP} = 8.4$ Hz, PCH_3), 1.60 (d, $J_{HP} = 8.7$ Hz, PCH_3), 2.81 (s, $C(O)CH_3$). $^{31}P\{^1H\}$-NMR (CD_2Cl_2): δ −5.5 (dd, $J_{PP} = 165$, 17 Hz, PMe_3), 47.1 (dd, $J_{PP} = 165$, 17 Hz, dmpe), 51.8 (t, $J_{PP} = 17$ Hz, dmpe). $[Mo(\eta^2\text{-}C(O)CH_3)(CO)(dmpe)_2]Cl$ (**5**). IR (CH_2Cl_2, cm^{-1}): ν(CO) 1817 (s), 1520 (m). ^1H-NMR (CD_2Cl_2): δ 0.79 (d, $J_{HP} = 5.1$ Hz, PCH_3), 1.25 (d, $J_{HP} = 5.5$ Hz, PCH_3), 1.36 (d, $J_{HP} = 7.0$ Hz, PCH_3), 1.60 (d, $J_{HP} = 8.0$ Hz, PCH_3), 1.66 (d, $J_{HP} = 8.9$ Hz, PCH_3), 1.7 (brs, 2 PCH_2), 1.83 (d, $J_{HP} = 5.0$ Hz, PCH_3), 1.85 (d, $J_{HP} = 7.7$ Hz, PCH_3), 1.89 (d, $J_{HP} = 8.6$ Hz, PCH_3), 2.92 (s, $C(O)CH_3$). $^{13}C\{^1H\}$-NMR (CD_2Cl_2): δ 9.8 (d, $J_{CP} = 17$ Hz, PCH_3), 13.7 (d, $J_{CP} = 25$ Hz, PCH_3), 14.6 (d, $J_{CP} = 22$ Hz, PCH_3), 14.7 (d, $J_{CP} = 17$ Hz, PCH_3), 16.0 (d, $J_{CP} = 19$ Hz, PCH_3), 18.0 (d, $J_{CP} = 16$ Hz, PCH_3), 20.1 (d, $J_{CP} = 25$ Hz, PCH_3), 20.3 (d, $J_{CP} = 23$ Hz, PCH_3), 27.1 (dd, $J_{CP} = 25$, 13 Hz, PCH_2), 28.6, 29.9, 30.6 (m, 3 PCH_2), 28.1 (s, $C(O)CH_3$), 225.3 (dq, $J_{CP} = 45$, 9 Hz, CO), 270.9 (dq, $J_{CP} = 35$, 6 Hz, $C(O)CH_3$). $^{31}P\{^1H\}$-NMR (CD_2Cl_2): δ 15.7 (t, $J_{PP} = 16$ Hz), 29.5 (dd, $J_{PP} = 50$, 33 Hz), 38.6 (td, $J_{PP} = 33$, 16 Hz), 52.7 (ddd, $J_{PP} = 50$, 33, 16 Hz).

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