least-squares cycle, the largest parameter shift was 0.02 times its estimated esd. Phenyl hydrogen atom positions were calculated (d_{C-H} set at 0.95 Å) and included in structure factor calculations but were not refined. The final difference Fourier map revealed an electron density peak in the region where the η^2-H_2 ligand was expected. The maximum in this area was positioned 1.6 Å from the Os atom approximately trans to O1 (O1–Os–peak = 170°). Other relevant angles about Os to this peak were 86° to P1, 80° to P2, 88° to P3 and 129° to O2. Attempts to refine this peak as a hydrogen atom or as a η^2-H_2 ligand were unsuccessful and upon careful examination of the electron density in this region, contours expected for a H_2 ligand were not observed. It was concluded that the presence of the heavy atoms in the structure precluded its resolution. The largest peaks in the final difference Fourier map were located approximately 0.9 Å from the Os atom and were about 2 electron Å^{-3}, compared with 0.9 electron Å^{-3} for the suspected η^2-H_2.

The final positional and thermal parameters of the refined atoms appear in Table IV. A table of observed and calculated structure factor amplitudes is available as supplementary material.

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Registry No. **1**, 113220-61-4; **3**, 113220-59-0; **4**, 113250-53-6; **5**, 113250-56-9; **6**, 113220-65-8; $(Ph_3P)_2Ru(CO)_2(OAc)_2$, 31267-49-9; $H_2C(SO_2CF_3)_2$, 428-76-2; $(Ph_3P)_2RuH(CO)(OAc)$, 50661-73-9; $(Ph_3P)_2Ru(CO)Cl(OAc)$, 34808-05-4; $(Ph_3P)_3OsH(OAc)$, 50894-84-3; $[(Ph_3P)_3Os(\eta^2\text{-HD})(\eta^2\text{-OAc})][PhC(SO_2CF_3)_2]$, 113220-63-6; $PhCD(SO_2CF_3)_2$, 113250-57-0.

Supplementary Material Available: Tables of positional and thermal parameters (complete listing), general temperature factor expressions, and distances and angles within the phenyl rings, $HC(SO_2CF_3)_2^-$ anion, and toluene solvate molecule (13 pages); a table of observed and calculated structure factor amplitudes (49 pages). Ordering information is given on any current masthead page.

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(27) Cromer, D. T.; Ibers, J. A. In ref 26.

Contribution from the Departamento de Química Inorgánica, Facultad de Química, Universidad de Sevilla,
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Synthesis, Characterization, and Properties of the η^2-Acyl Complexes $Mo(\eta^2\text{-}COCH_2CMe_3)X(PMe_3)_4$ (X = Cl, Br)

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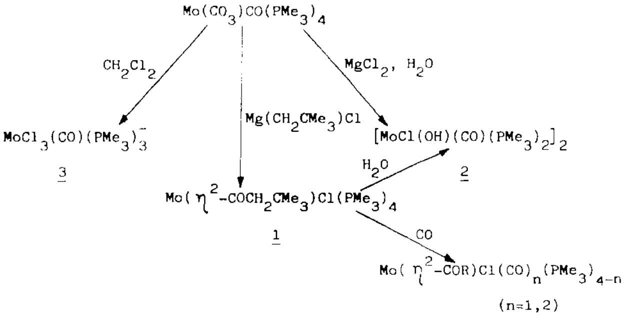
The η^2-acyl complexes of molybdenum $Mo(\eta^2\text{-}COCH_2CMe_3)X(PMe_3)_4$ (X = Cl (**1a**), Br (**1b**)) have been prepared by the action of $Mg(CH_2CMe_3)X$ on the carbonyl carbonate $Mo(CO_3)(CO)(PMe_3)_4$. Complex **1** decomposes in solution with dissociation of PMe_3. This reaction occurs faster in the presence of small amounts of water (2–3 drops) with formation of the hydroxo species $[MoX(CO)(PMe_3)_2(\mu\text{-}OH)]_2$ (X = Cl (**2a**), Br (**2b**)). Carbonylation of **1a**, at room temperature and pressure, affords successively $Mo(\eta^2\text{-}COCH_2CMe_3)Cl(CO)(PMe_3)_3$ and $Mo(\eta^2\text{-}COCH_2CMe_3)Cl(CO)_2(PMe_3)_2$. Finally, the reaction of $Mo(CO_3)(CO)(PMe_3)_4$ with CH_2Cl_2 yields the 7-coordinate anionic compound $MoCl_3(CO)(PMe_3)_3$, which is isolated as the tetramethylphosphonium salt, $[PMe_4][MoCl_3(CO)(PMe_3)_3]$ (**3**). The crystal structure of **1b** has been determined by X-ray crystallography. It crystallizes in the orthorhombic space group, $P2_12_12_1$, with a = 10.021 (2) Å, b = 16.752 (3) Å, c = 16.855 (5) Å, and D_{calcd} = 1.36 g cm^{-3} for Z = 4. A total of 1098 independent observed [$F_o \geq 5\sigma(F_o)$] reflections were used in the least-squares refinement, which led to a final conventional R value of 0.051. The molybdenum atom has an approximate pentagonal-bipyramidal geometry, the η^2-acyl ligand residing in the pentagonal plane. The acyl and bromo ligands are trans; important distances include Mo–Br = 2.687 (5) Å, Mo–C = 2.00 (3) Å, Mo–O = 2.21 (2) Å, and Mo–P = 2.48 (4) Å, average.

Introduction

η^2-Acyl complexes of molybdenum have been relatively uncommon until very recently, the first compound of this type being the chloride-bridged, dinuclear species $[Mo(\eta^2\text{-}COCH_2SiMe_3)(CO)_2(PMe_3)(\mu\text{-}Cl)]_2$.[2] Later work from our laboratory has resulted in the characterization of the formally 6-coordinate mononuclear complexes $Mo(\eta^2\text{-}COR)X(CO)(PMe_3)_3$ and of other related compounds,[3] while the groups of Lalor and Ferguson,[4] Curtis,[5] and Templeton[6] have effected the characterization of the complexes $TpMo(\eta^2\text{-}COR)(CO)_2$ (Tp = hydridotris(pyrazolyl)borate ligand) and of other similar species.

Scheme I



We are currently studying[7] the influence of steric and electronic effects on the relative stability of 7-coordinate alkyl carbonyl complexes, LnM(CO)R, and isomeric 6-coordinate η^2-acyls,

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[1] (a) Universidad de Sevilla. (b) Northern Illinois University.

[2] Carmona, E.; Wilkinson, G.; Rogers, R. D.; Hunter, W. D.; Zawarotko, M. J.; Atwood, J. L. *J. Chem. Soc., Dalton Trans.* **1980**, *229*.

[3] Carmona, E.; Sânchez, L.; Marín, J. M.; Poveda, M. L.; Atwood, J. L.; Priester, R. D.; Rogers, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 3214.

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[6] Rusik, C. A.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 4652.

[7] Carmona, E.; Sânchez, L., to be submitted for publication.

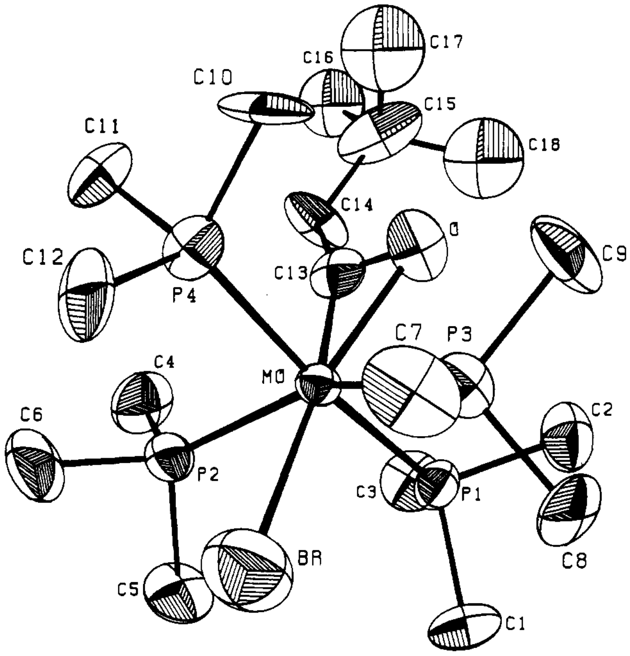

Figure 1. Molecular structure and atom-labeling scheme for $Mo(\eta^2\text{-}COCH_2CMe_3)Br(PMe_3)_4$. The atoms are represented by their 50% probability ellipsoids for thermal motion. C(16)–C(18) were refined isotropically; hydrogen atoms were not located. Important parameters: Mo–Br = 2.687 (5) Å, Mo–P = 2.48 (4) Å average, Mo–C(13) = 2.00 (3) Å, Mo–O = 2.21 (2) Å, C(13)–O = 1.32 (3) Å, Mo–C(13)–O = 81 (2)°, Mo–C(13)–C(14) = 157 (2)°, Mo–O–C(13) = 63 (1)°.

$LnM(\eta^2\text{-}COR)$, for M = Mo and W. The results found to date indicate that, for the molybdenum complexes, the η^2-acyl structure is favored over the alkyl carbonyl alternative. In this paper, we wish to report the synthesis of a new, unusual type of η^2-acyl complex of molybdenum, $Mo(\eta^2\text{-}COCH_2CMe_3)X(PMe_3)_4$ (X = Cl (**1a**), Br (**1b**)), its crystal structure, and its reaction with CO.

Results and Discussion

The transformations observed in this study are summarized in Scheme I.

We have previously reported that the alkylation of the chlorocarbonyl complex $MoCl_2(CO)_2(PMe_3)_3$ with various Grignard or organolithium reagents produces[3] the η^2-acyl complexes $Mo(\eta^2\text{-}COR)Cl(CO)(PMe_3)_3$ (R = CH_3, CH_2SiMe_3, CH_2CMe_3, CH_2CMe_2Ph). These compounds react with carbon monoxide, under ambient conditions, to yield the η^2-acyl dicarbonyl complexes $Mo(\eta^2\text{-}COR)Cl(CO)_2(PMe_3)_2$. The use of the carbonyl carbonate compound $Mo(CO_3)(CO)(PMe_3)_4$, obtained by a metal-induced reductive disproportionation of CO_2,[8] has now allowed the preparation of the η^2-acyl complexes $Mo(\eta^2\text{-}COCH_2CMe_3)X(PMe_3)_4$ (X = Cl (**1a**), Br (**1b**)). When the above carbonate is stirred with 1.5–2 equiv of $Mg(CH_2CMe_3)X$ in Et_2O, a dark red solution of compound **1** is formed. Complex **1** is a new member of the series of η^2-acyls of composition $Mo(\eta^2\text{-}COR)Cl(CO)_n(PMe_3)_{4-n}$, and it is a rather unusual compound since it is the only known η^2-acyl of a group 6 metal, which is not stabilized by the presence of the strong π-acid carbonyl ligand. Complex **1** can be isolated as dark red crystals, which are very air and moisture sensitive, particularly in solution. While **1** is indefinitely stable as a solid, solutions of complex **1** when kept under dinitrogen are unstable at room temperature and decompose readily, with dissociation of PMe_3. This has precluded full characterization of the complex by NMR studies. Metathetical replacement of the chloride ligand of **1a** by bromide, in the presence of PMe_3, takes place easily, with formation of **1b**. In the absence of added trimethylphosphine, the decomposition of **1** is facile, especially in small amounts of water, which generate a yellow hydroxo species formulated as the dimer $[MoX(CO)(PMe_3)_2(\mu\text{-}OH)]_2$ (X = Cl (**2a**), Br (**2b**)) on the basis of analytical and spectroscopic data (see Experimental Section). The same complex can be obtained by the action of MgX_2 on the carbonyl carbonate complex $Mo(CO_3)(CO)(PMe_3)_4$, in the presence of water (2–3 drops).

Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

cmpd	$Mo(\eta^2\text{-}COCH_2CMe_3)Br(PMe_3)_4$
color/shape	red/parallelepiped
mol wt	579.3
space group	$P2_12_12_1$
temp, °C	22
cell constants[a]	
a, Å	10.021 (2)
b, Å	16.752 (3)
c, Å	16.855 (5)
cell vol, Å^3	2829.5
molecules/unit cell	4
d_{calcd}, g cm^{-3}	1.36
μ(calcd), cm^{-1}	20.1
diffractometer/scan	Enraf-Nonius CAD4/θ–2θ
range of rel transm factors, %	97/100 (not cor)
radiation, graphite monochromator	Mo Kα (λ = 0.71073 Å)
Max crystal dimens, mm	0.50 × 0.60 × 0.65
scan width	0.80 + 0.35 tan θ
std reflcns	(600), (0,10,0), (0,0,10)
decay of stds	±2%
no. of reflcns measured	1618
2θ range, deg	$2 \le 2\theta \le 40$
range of *h,k,l*	+9,+16,+16
no. of reflcns obsd [$F_o \ge 5\sigma(F_o)$][b]	1098
computer programs[c]	SHELX[14]
structure soln[d]	heavy-atom techniques
no. of params varied	211
weights	unit
GOF	4.59
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.051
R_w	0.069
R inverse confign	0.062
largest feature in final diff map, e Å^{-3}	0.3

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 20 reflections θ > 14°. [b] Corrections: Lorentz and polarization. [c] Neutral-atom scattering factors and anomalous dispersion corrections from ref 15. [d] High thermal motion was noted for the neopentyl methyl groups; however, it was not possible to refine or resolve a disorder model and these atoms (C(16)–C(18)) were refined isotropically only. No hydrogen atoms were included. Positional parameters are given in Table II.

The presence of the η^2-acyl linkage in the molecules of **1** can be inferred from IR studies, which show the existence of a medium-intensity absorption at 1425 cm^{-1} (KBr). This band can be assigned to ν(C–O) of the η^2-acyl ligand, and it is one of the lowest frequencies yet reported for an η^2-acyl unit, clearly below the normal region of 1600–1450 cm^{-1}, where this group is generally found to absorb.[9] This low frequency, which indicates a high electron density at the metal center, is presumably due to the presence of the four strong electron-releasing PMe_3 ligands and to the absence of carbonyl groups. The ^{1}H NMR spectrum of **1** is complicated by the presence of signals due to dissociated PMe_3 and to other species resulting therefrom and therefore provides no definite information with regard to its structure. No exchange between coordinated and free PMe_3 takes place in solution on the NMR time scale, and this allows us to obtain valuable information on the geometry of the molecules of **1** from ^{13}C and ^{31}P NMR studies carried out in the presence of added PMe_3 (1–2 equiv). The observations of a singlet in the ^{31}P{^{1}H} NMR spectrum and a pseudoquintet in the ^{13}C NMR spectrum for the PMe_3 groups indicate the equivalence of the four phosphine ligands, and hence a distorted octahedral structure for **1**, with the η^2-acyl and the halide ligands occupying mutually trans positions.

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(8) Carmona, E.; González, F.; Poveda, M. L.; Marín, J. M.; Atwood, J. L.; Rogers, R. D. *J. Am. Chem. Soc.* **1983**, *105*, 3365.

(9) See, for instance: Hitam, R. B.; Narayanaswamy, R.; Rest, A. J. *J. Chem. Soc., Dalton Trans.* **1980**, 615.

Table II. Final Fractional Coordinates for $Mo(\eta^2\text{-}COCH_2CMe_3)Br(PMe_3)_4$

atom	x/a	y/b	z/c	U(eqv)[a]
Mo	0.5595 (2)	0.9440 (1)	0.1322 (1)	0.031
Br	0.3897 (5)	0.8212 (3)	0.1503 (3)	0.113
P(1)	0.3983 (7)	1.0272 (4)	0.0615 (4)	0.043
P(2)	0.4421 (9)	0.9714 (4)	0.2611 (4)	0.049
P(3)	0.6009 (8)	0.8619 (4)	0.0091 (5)	0.049
P(4)	0.7433 (9)	0.8766 (4)	0.2009 (5)	0.050
O	0.714 (2)	1.016 (1)	0.074 (1)	0.065
C(1)	0.231 (3)	0.988 (2)	0.031 (2)	0.068
C(2)	0.453 (4)	1.070 (2)	−0.034 (2)	0.071
C(3)	0.351 (3)	1.124 (2)	0.103 (2)	0.064
C(4)	0.475 (3)	1.056 (2)	0.316 (2)	0.079
C(5)	0.255 (3)	0.974 (2)	0.259 (2)	0.072
C(6)	0.458 (4)	0.898 (2)	0.341 (2)	0.081
C(7)	0.635 (4)	0.757 (2)	0.021 (2)	0.073
C(8)	0.469 (3)	0.853 (2)	−0.064 (2)	0.069
C(9)	0.742 (4)	0.893 (2)	−0.055 (2)	0.079
C(10)	0.905 (2)	0.870 (2)	0.143 (2)	0.074
C(11)	0.817 (3)	0.922 (2)	0.286 (2)	0.071
C(12)	0.719 (4)	0.770 (2)	0.236 (2)	0.077
C(13)	0.668 (2)	1.042 (2)	0.143 (2)	0.048
C(14)	0.719 (3)	1.117 (2)	0.180 (2)	0.063
C(15)	0.832 (3)	1.162 (2)	0.136 (3)	0.085
C(16)	0.864 (4)	1.238 (2)	0.197 (2)	iso
C(17)	0.950 (5)	1.115 (3)	0.121 (3)	iso
C(18)	0.794 (5)	1.188 (3)	0.053 (3)	iso

[a] U(eqv) is equal to $(U_{11} + U_{22} + U_{33})/3$.

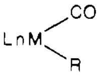
The above assumption regarding the geometry of **1** has been confirmed by X-ray studies carried out on complex **1b** (Table I). The structure of **1b** is presented in Figure 1. The overall geometry of the molecule can be considered to be a very distorted octahedral geometry with the bromo and acyl ligands trans; however, P(1)–P(4) are planar only to within 0.4 Å. Alternatively, if C(13) and O are considered as separate ligands, a pentagonal-bipyramidal description of the structure can be employed. The pentagonal plane containing C(13), O, P(3), Br, and P(2) is planar to within 0.012 Å with Mo 0.006 Å out of this mean plane. In this description the variation in Mo–P distances appears related directly to different ligand sites. P(2) and P(3) in equatorial sites are an average 2.518 (6) Å from Mo, while the two axial ligands P(1) and P(4) average 2.447 (4) Å from Mo. The combined average Mo–P separation for all four phosphine ligands is 2.48 (4) Å, close to the 2.49 (1) Å observed in *trans*-$[Mo(\eta^2\text{-}C_2H_4)_2(PMe_3)_4]$.[10]

The same geometry observed in the title complex was found for $Mo(\eta^2\text{-}HC_2Ph)Br_2(CO)(PEt_3)_2$[11] with phosphine ligands occupying the axial positions. In this latter complex the equatorial Mo–Br separations averaged 2.69 (1) Å compared to the Mo–Br distance of 2.687 (5) Å observed in **1b**.

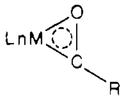
The acyl portion of the molecule is planar to within 0.004 Å (Mo, O, C(13), C(14)) with C(15) 0.08 Å out of this plane. The dihedral angle between the pentagonal plane about Mo and the plane defined by the acyl ligand is only 1.0°. In $Mo(\eta^2\text{-}COCH_2SiMe_3)Cl(CO)(PMe_3)_3$[3] and $[Mo(\eta^2\text{-}COCH_2SiMe_3)Cl(CO)_2(PMe_3)]_2$[2] the geometry at molybdenum was observed to be more nearly octahedral, with dihedral angles of 26.95 and 32.39°, respectively, between the planes defined by the acyl linkage and Mo and the three other ligands in the square plane. In the title compound the Mo–C(13) separation is 2.00 (3) Å, within 3σ of similar distances in $Mo(\eta^2\text{-}COCH_2SiMe_3)Cl(CO)(PMe_3)_3$ (2.024 (6) Å) and $[Mo(\eta^2\text{-}COCH_2SiMe_3)Cl(CO)_2(PMe_3)]_2$ (2.023 (3) Å); however, the Mo–O distance is significantly shorter (2.21 (2) Å versus 2.324 (4) and 2.292 (2) Å, respectively), indicating a stronger interaction.

As expected, the carbonylation of **1a** does not lead to a change in the bonding mode of the acyl ligand, but rather to substitution of one of the PMe_3 ligands by a molecule of CO, with formation of $Mo(\eta^2\text{-}COCH_2CMe_3)Cl(CO)(PMe_3)_3$.[3] Further reaction with CO yields the dicarbonyl derivative $Mo(\eta^2\text{-}COCH_2CMe_3)Cl(CO)_2(PMe_3)_2$. These reactions imply simply the substitution of one and two basic PMe_3 ligands, respectively, by the strong π-acid CO, without change in the η^2-acyl linkage, and must therefore be accompanied by a substantial decrease in the electron density at the metal center. This is clearly shown by the large shift to high frequency observed for $\nu(C\text{–}O)_{acyl}$ in the series of complexes $Mo(\eta^2\text{-}COCH_2CMe_3)Cl(CO)_n(PMe_3)_{4-n}$: $n = 0$, 1425 cm^{-1}; $n = 1$, 1525 cm^{-1}; $n = 2$, 1575 cm^{-1}. Since the metal to η^2-acyl bond can be formally regarded as a multiple interaction involving the acyl carbon (σ interaction) and C=O bond (σ and π), the observed shift is in accord with a decrease in the π-back-donation from the filled $d\pi$ metal orbitals to the empty π^* orbital of the C=O unit, which is to be expected upon substitution of PMe_3 by CO.

Some comments on the electronic and steric characteristics of the η^2-acyl linkage in **1** are pertinent at this moment. Recent work carried out in our laboratory has shown[7] the influence of the steric and electronic effects in the relative stabilities of the 7-coordinate alkyl carbonyl formulation, A, and the isomeric 6-coordinate η^2-acyl structure, B, in a series of related complexes of molybdenum and tungsten, LnM(CO)R and LnM(η^2-COR). For M = Mo, the η^2-acyl structure is favored over the alkyl carbonyl for all the complexes investigated, except for the acetyl compound $Mo(COCH_3)(S_2CNMe_2)(CO)(PMe_3)_2$, in which the 18-electron configuration is attained by virtue of a strong Mo–C–H interaction involving one of the acetyl carbon–hydrogen bonds. The presence of an η^2-acyl and four PMe_3 ligands in the molecule of **1** suggests the existence of a relatively high electron density at the molybdenum center (see above). Although this would favor the alkyl carbonyl structure A,[7] this formulation seems very unlikely in the present case on steric grounds. As already mentioned, complex **1** decomposes readily by dissociation of PMe_3, and it is probable that either compound **1** or, more likely, the species resulting from the dissociation of PMe_3 is in equilibrium with the isomeric alkyl carbonyl, which would react quickly with water to give **2**. Attempts to prepare analogues of **1** with the groups CH_2SiMe_3 and CH_2CMe_2Ph have proved unsuccessful. Although stirring a suspension of $Mo(CO_3)(CO)(PMe_3)_4$ in Et_2O with 1.5–2 equiv of the corresponding Mg(R)Cl results in dissolution of the suspended solid, no tractable products can be isolated. Workup of these reactions is long and difficult and provides only small amounts of the hydroxo complex **2**, formed possibly by the action of adventitious water on an unstable alkyl carbonyl complex, as described above for the neopentyl derivative.



A



B

During the above studies aimed at the alkylation of the blue $Mo(CO_3)(CO)(PMe_3)_4$ complex, it was found that its solutions in dichloromethane slowly deposit a yellow-orange powder. The IR spectrum of this solid displays a strong absorption at 1750 cm^{-1}, attributable to a carbonyl ligand, but no bands in the region 1600–1500 cm^{-1} characteristic of the carbonate ligand in this type of complex[8] (1600 cm^{-1} in $Mo(CO_3)(CO)(PMe_3)_4$). The new compound, designated as **3**, is insoluble in common organic solvents, and this and the presence of a strong absorption at 990 cm^{-1} suggest its formulation as the phosphonium salt of an anionic molybdenum complex. In accord with this, solutions of **3** in acetone–water mixtures show two ^{31}P NMR resonances at 37 and 24.5 ppm, which can be respectively assigned to the phosphonium cation, $[PMe_4]^+$, and to coordinated PMe_3. Furthermore, action of CO on a THF suspension of **3** produces a yellow precipitate of $[PMe_4]Cl$ and a yellow solution from which the known complex $MoCl_2(CO)_2(PMe_3)_3$[12] can be isolated. Preliminary crystallo-

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[10] Carmona, E.; Marín, J. M.; Poveda, M. L.; Atwood, J. L.; Rogers, R. D. *J. Am. Chem. Soc.* **1983**, *105*, 3015.

[11] Winston, P. B.; Burgmayer, S. J. N.; Templeton, J. L. *Organometallics* **1983**, *2*, 167.

[12] Carmona, E.; Doppert, K.; Marín, J. M.; Poveda, M. L.; Sánchez, L.; Sánchez-Delgado, R. *Inorg. Chem.* **1984**, *23*, 530.

graphic studies have confirmed the ionic nature of this compound;[3] however, complex disorder of the anion has thus far precluded a complete structural investigation.

Experimental Section

Microanalyses were by Pascher Microanalytical Laboratory, Bonn. Infrared spectra were recorded on Perkin-Elmer Models 577 and 684 spectrophotometers. ^{1}H, ^{31}P, and ^{13}C NMR spectra were run on a Varian XL-200 spectrometer. ^{31}P shifts were measured with respect to external 85% H_3PO_4. ^{13}C NMR spectra were referenced by using the ^{13}C resonance of the solvent as an internal standard but are reported with respect to $SiMe_4$.

All preparations and other operations were carried out under oxygen-free nitrogen, following conventional Schlenk techniques. Solvents were dried and degassed before use. The petroleum ether used had a boiling point range of 40–60 °C. The compound Mo(CO$_3$)(CO)(PMe$_3$)$_4$[8] and the ligand PMe$_3$[13] were prepared according to literature methods. Details of the preparation of the carbonate complex are given below.

Synthesis of Mo(CO$_3$)CO(PMe$_3$)$_4$. A solution of the complex *cis*-Mo(N$_2$)$_2$(PMe$_3$)$_4$ (0.68 g, 1.5 mmol) in 20 mL of tetrahydrofuran was reacted with carbon dioxide (4 atm), in the presence of trimethylphosphine (0.1 mL, ca. 1 mmol). After 24 h of standing at room temperature, dark blue crystals of the desired complex were obtained. The crystals were filtered off, washed with 2 × 5 mL of Et$_2$O, and dried under vacuum. Yield: 0.62 g, 1.3 mmol, ca. 85%.

Synthesis of Mo(η^2-COCH$_2$CMe$_3$)Cl(PMe$_3$)$_4$ (1). To a stirred suspension of blue Mo(CO$_3$)(CO)(PMe$_3$)$_4$ (0.49 g, ca. 1 mmol) in 25 mL of diethyl ether, at 0 °C, were added free PMe$_3$ (0.2 mL, ca. 2 mmol) and Mg(CH$_2$CMe$_3$)Cl (4.0 mL of a ca. 0.50 M Et$_2$O solution). The cold bath was then removed and the mixture stirred at room temperature for 4–6 h. After centrifugation, the solvent was evaporated in vacuo and the dark red residue was then treated with 0.2 mL of free PMe$_3$ and 20 mL of petroleum ether. The mixture was centrifuged and the title product crystallized by cooling overnight at −30 °C. Yield: ca. 40%. IR (KBr disk): 1425 (ν(CO)), 1290, 1270, 940 cm^{-1}. ^{31}P{^{1}H} NMR (C$_6$D$_6$, 20 °C): δ −2.3 (s). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 19.89 (pseudoquintet, PMe$_3$, $^2J_{\mathrm{app}}$(C–P) = 5 Hz), 30.00 (s, CH$_2$C*Me*$_3$), 57 (s, *C*H$_2$CMe$_3$). Anal. Calcd for Mo(COCH$_2$CMe$_3$)Cl(PMe$_3$)$_4$: C, 40.5; H, 8.8. Found: C, 39.5; H, 8.7. If activation of the Mg turning used for the synthesis of the Grignard reagent is accomplished by addition of 1,2-dibromoethane, mixtures of **1a** and **1b** are obtained. Complex **1b** can be prepared and isolated by a procedure similar to that described for **1a**, by carrying out the reaction in the presence of ca. 2 equiv of MgBr$_2$. ^{31}P{^{1}H} NMR: δ 1.56 (s).

Carbonylation of Complex 1. Through a solution of **1** (0.53 g, ca. 1 mmol) in petroleum ether (40 mL) was bubbled carbon monoxide at room temperature until the color of the solution changed from dark red to pale yellow (ca. 2 h). Yellow microcrystals of Mo(η^2-COCH$_2$CMe$_3$)Cl(CO)$_2$(PMe$_3$)$_2$ were obtained in ca. 70% yield upon cooling at −30 °C. The monocarbonyl complex Mo(η^2-COCH$_2$CMe$_3$)Cl(CO)(PMe$_3$)$_3$ is the main species in solution after a reaction time of ca. 45 min, as shown by solution infrared studies.

Synthesis of [MoX(CO)(PMe$_3$)$_2$(μ-OH)]$_2$ (2). Two methods are provided:

(a) To a solution of **1** (0.53 g, ca. 1 mmol) in 40 mL of petroleum ether was added some water (2–3 drops), and the mixture was stirred at room temperature. After 3–4 h a yellow solid was formed, which was filtered off, washed with Et$_2$O, and dried in vacuo. Yield: 50–60%.

(b) To a suspension of Mo(CO$_3$)(CO)(PMe$_3$)$_4$ (0.49 g, ca. 1 mmol) in 40 mL of THF were added MgBr$_2$ (10 mL of a recently prepared 0.2 N solution in Et$_2$O, ca. 2 mmol) and 2–3 drops of water. Upon stirring at room temperature for 2 h, an orange solution of [MoBr(CO)(PMe$_3$)$_2$(μ-OH)]$_2$ was obtained. Complex **2** can be recrystallized from CH$_2$Cl$_2$–toluene. IR (KBr disk): bands at 3300–3200 (broad, O–H), 1740 (C–O), 1640, and 940 cm^{-1} (PMe$_3$). ^{31}P{^{1}H} NMR (C$_4$H$_8$O–C$_6$D$_6$ external reference) δ 18.7 (s). Anal. Calcd for [MoBr(CO)(PMe$_3$)$_2$(OH)]$_2$: C, 22.5; H, 5.09. Found: C, 22.72; H, 5.64.

Synthesis and Carbonylation of [PMe$_4$][MoCl$_3$(CO)(PMe$_3$)$_3$] (3). A solution of the complex Mo(CO$_3$)(CO)(PMe$_3$)$_4$ (0.5 g, ca. 1 mmol) in a 2:1 mixture of CH$_2$Cl$_2$–THF was set aside without stirring for 2 or 3 days. Yellow-orange crystals of the title product were obtained in low yield (30–35% referred to Mo). IR (Nujol mull): 1750 (C–O), 990 (PMe$_4^+$), 945 (PMe$_3$). ^{31}P{^{1}H} NMR (acetone–water, 20 °C): δ 24.5 (s, relative intensity 3, PMe$_3$), 37 (s, relative intensity 1, PMe$_4^+$).

Anal. Calcd for [PMe$_4$][MoCl$_3$(CO)(PMe$_3$)$_3$]: C, 30.6; H, 7.10. Found: C, 30.4; H, 7.01.

A suspension of complex **3** (0.44 g, ca. 0.8 mmol) in 40 mL of THF was stirred under CO, at room temperature and pressure, for a period of 10 h, during which the solid was slowly taken into solution. After centrifugation of the resulting green solution, the solvent was removed in vacuo, and a yellow solid was obtained that was identified by IR and ^{31}P NMR studies as the complex MoCl$_2$(CO)$_2$(PMe$_3$)$_3$.

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Supplementary Material Available: Tables of thermal parameters and least-squares-plane results (3 pages); a listing of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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