photophysics of these molecules. A better understanding of the structural and electronic features of these molecules will also be pursued.

Conclusions

The preparation of several new diplatinum complexes containing μ-phenylethenylidene ligands is reported. X-ray structural determinations of three of these compounds confirm unambiguously the molecular structures of two new classes of diplatinum halide complexes. Theoretical calculations indicate that the electronic structure of these molecules might be similar to that found previously for $Pt_2(POP)_4^{4-}$. Study of the photochemistry and photophysical properties of several of these organometallic, diplatinum compounds reveals that selected compounds act as photochemical catalysts in the conversion of 2-propanol to acetone and molecular hydrogen and participate in halide to metal atom-transfer reactions under photolytic conditions. One complex emits a strong visually perceptible luminescence at 77 K when excited with radiation of 410 nm.

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Registry No. **1a**, 106357-35-1; **1b**, 106357-37-3; **2**, 122236-05-9; **3**, 122236-06-0; **4**, 122236-07-1; **5** (thiocyanate), 122236-15-1; **5** (isothiocyanate), 122236-16-2; **6**, 122236-08-2; **7**, 122236-09-3; **8**, 122236-10-6; **9**, 122236-11-7; **10**, 122236-12-8; **11**, 122236-13-9; **12**, 122236-14-0; $NaSC_6Cl_5$, 22441-28-7; isopropyl mercaptan, 75-33-2; lithium isopropylthiolate, 16203-41-1; lithium thiophenolate, 2973-86-6; thiophenol, 108-98-5.

Supplementary Material Available: Tables of final atomic positional and thermal parameters, interatomic distances and angles, and selected least-squares planes data (30 pages); listings of final observed and calculated structure factors for the X-ray structures of compounds 2, 4, and 10 (98 pages). Ordering information is given on any current masthead page.

Formation of Carboxylate Complexes from the Reactions of CO_2 with Ethylene Complexes of Molybdenum and Tungsten. X-ray and Neutron Diffraction Studies

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Carbon–carbon bond formation by coupling of ethylene with carbon dioxide on the coordination sphere of the metal center in the electron-rich complexes *trans*-$M(C_2H_4)_2(PMe_3)_4$ (M = Mo, **1**; M = W, **2**) can be effected under mild conditions by reactions of **1** and **2** with CO_2. These afford the binuclear hydrido acrylate derivatives $[MH(OOCCH{=}CH_2)(C_2H_4)(PMe_3)_2]_2$ (M = Mo, **3**; M = W, **4**), which contain bridging μ_2-η^3,η^1-acrylate ligands. Hydrogenation of **3** and **4** in the presence of PMe_3 provides the hydrido propionates $MoH(\eta^2\text{-}OOCCH_2CH_3)(PMe_3)_4$ (**5**) and $WH_3(\eta^1\text{-}OOCCH_2CH_3)(PMe_3)_4$ (**6**), but the direct reaction of **1** and **2** with a 1:1 mixture of CO_2/H_2 yields instead the hydrido carbonate derivatives $MH_2(\eta^2\text{-}CO_3)(PMe_3)_4$ (M = Mo, **7**; M = W, **8**). The hydrido allyl compounds $MH(\eta^3\text{-}C_3H_5)(PMe_3)_4$ (M = Mo, **9**; M = W, **10**), formed by sodium amalgam reduction of $MCl_4(PMe_3)_3$ under propylene, do not react with CO_2 with carbon–carbon bond formation but rather with reductive elimination of propylene and production of the adduct *trans*-$Mo(CO_2)_2(PMe_3)_4$ and various carbonate complexes. The crystal and molecular structures of **3**, **4**, and **6** have been determined by X-ray studies, and, in addition, a low-temperature (20 K) neutron diffraction analysis of **4** has been performed. **3** is monoclinic, $P2_1/n$, with a = 12.117 (8) Å, b = 15.072 (5) Å, c = 17.700 (5) Å, β = 102.18 (3)°, Z = 4, and R = 0.032, while **6** is monoclinic, $P2_1/c$, with a = 12.813 (2) Å, b = 8.903 (3) Å, c = 21.671 (3) Å, β = 88.62 (1)°, Z = 4, and R = 0.048. The crystal of **4** used for the neutron diffraction study is monoclinic, $P2_1/c$, with a = 14.23 (1) Å, b = 11.80 (1) Å, c = 20.58 (2) Å, β = 104.94 (6)°, Z = 4, and R = 0.034.

Carbon dioxide is an attractive and potentially useful C1 synthetic unit, but its scarce reactivity toward unsaturated organic fragments and its reluctance to undergo economically useful transformations promoted by transition metals constitute major drawbacks for its exploitation as a source of elemental carbon. Despite this inertia of carbon dioxide, many interesting reactions have been discovered in the last two decades,[2] and it is now widely

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recognized that CO_2 can be activated by transition-metal fragments. Among the most important transformations in carbon dioxide chemistry are those reactions leading to carbon–carbon bond formation, mainly insertion into M–C bonds, oxidative coupling with unsaturated organic molecules, and insertion into C–H bonds.[2] Of these, the latter is particularly attractive since its involves both C–H bond cleavage and C–C bond formation, two of the most intriguing problems in the application of transition-metal compounds to the synthesis of industrially important organic molecules. Nevertheless, this process has so far been observed only for systems containing activated C–H bonds.[3,4]

The coupling reactions of CO_2 with molecules containing multiple bonds may be performed by systems that provide a low kinetic barrier for the desired transformation, and this can be made possible by (a) activation of CO_2, (b) activation of the organic fragment, or (c) simultaneous activation of both substrates. Activation of CO_2 is expected to occur upon coordination to an electron-rich transition-metal center, but many of the well-characterized $M{-}CO_2$ complexes do not undergo further reactions. This is, for instance, the case of the bis-adduct *trans*-$Mo(CO_2)_2(PMe_3)_4$, which contains strongly bound CO_2 displaying very limited reactivity.[5a]

As a continuation of previous work on transition-metal–carbon dioxide chemistry, we have investigated the reactivity of the ethylene complexes *trans*-$M(C_2H_4)_2(PMe_3)_4$ (M = Mo, 1;[5b] M = W, 2[5c]) toward CO_2. The electron-rich nature of the metal center in these compounds and the ready availability of a vacant coordination position by facile dissociation of one of the PMe_3 ligands[5b,c] make these compounds ideal candidates for CO_2 activation, simultaneous with C_2H_4 activation. Indeed, carbon–carbon bond formation by coupling of CO_2 with one of the coordinated ethylene molecules is observed, with formation of the binuclear complexes $[MH(OOCCH{=}CH_2)(C_2H_4)(PMe_3)_2]_2$ (M = Mo, 3; M = W, 4) which contain bridging acrylate ligands. The formation and spectroscopic characterization of these and other related products along with the study of their chemical reactivity are reported herein. Also reported are the results of X-ray studies carried out with compounds 3 and 4 and with the propionate derivative $WH_3(OOCCH_2CH_3)(PMe_3)_4$ (6) as well as a neutron diffraction analysis of the tungsten acrylate complex 4. Part of this work has appeared in preliminary form.[5d]

Results and Discussion

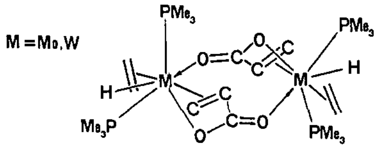
Synthesis of $[MH(OOCCH{=}CH_2)(C_2H_4)(PMe_3)_2]_2$ (M = Mo, 3; M = W, 4). The pale yellow solutions of the ethylene complexes 1 and 2 react with high purity commercial CO_2, under very mild conditions, to afford off-white crystalline materials of formulation $[MH(OOCCH{=}CH_2)(C_2H_4)(PMe_3)_2]_2$ (eq 1). The reactions are

$$\textit{trans}\text{-}M(C_2H_4)_2(PMe)_4 + CO_2 \rightarrow$$
$$\begin{array}{l}1{:}\ M = Mo\\ 2{:}\ M = W\end{array}$$
$$\tfrac{1}{2}[MH(OOCCH{=}CH_2)(C_2H_4)(PMe_3)_2]_2 + 2\,PMe_3 \quad (1)$$
$$\begin{array}{l}3{:}\ M = Mo\\ 4{:}\ M = W\end{array}$$

carried out in diethyl ether, at room temperature or below, by bubbling CO_2 through solutions of 1 or 2. Although complex 3 is fairly thermally stable once isolated in a pure state, extensive decomposition takes place during its formation and subsequent workup, and yields of isolated product are always below 30–35%. The reaction leading to 3 is not yet fully understood, and other side transformations, which are still under investigation, seem to occur simultaneously. For the tungsten system, however, the reaction takes place readily and yields of isolated, crystalline product are of the order of 60–70%.

Compounds 3 and 4 are moderately insensitive to air in a crystalline state but decompose readily in solution. They are soluble in tetrahydrofuran (THF) and aromatic hydrocarbons but decompose rapidly in chlorinated solvents, even under an atmosphere of dinitrogen. They are best crystallized from Et_2O, in which they are sparingly soluble. The binuclear formulation proposed for these compounds was demonstrated by a cryoscopic molecular weight determination carried out with Et_2O-free samples of 4.

Spectroscopic Properties of 3 and 4. The structural complexity of the molecules of 3 and 4 made full characterization of these compounds from the available spectroscopic data difficult, and the proposed bridging acrylate structure was determined from the results of single-crystal X-ray studies. Nevertheless, IR and NMR data are fully in agreement with the X-ray data, which means that the solid-state structure found for 3 and 4 (structure A) is maintained in solution. As discussed below, NMR data, particularly ^{13}C NMR studies, unambiguously demonstrate the occurrence of a carbon–carbon bond formation process, in a reaction which formally corresponds to the insertion of CO_2 into one of the ethylene C–H bonds.



A

In the IR spectrum of 3 and 4 a strong absorption is observed at ca. 1510 cm^{-1} (1480 cm^{-1} in a sample of 4*, 50% enriched in $^{13}CO_2$) that suggests the presence of a carboxylate group. ^1H and ^{13}C NMR studies demonstrate the presence of a hydride and of a carboxylate ligand in the molecules of 3 and 4, the latter being formed by coupling of CO_2 with one of the original ethylene molecules. Thus, there is a high-field signal (δ −6.1 and −1.1 ppm for 3 and 4, respectively) that can be attributed to a hydride ligand, although coupling to the ^{183}W nucleus ($I = {}^1/_2$, 14.3%) is not observed in the spectrum of 4. The $^{13}C\{^1H\}$ NMR spectrum displays, in addition to signals due to the PMe_3 ligands, a low-field resonance at ca. 175 ppm due to the carboxylate group and four olefinic signals at 55.1, 39.6, 38.3, and 32.8 ppm (data for 4). The signal at 55.1 ppm corresponds to a =CH– carbon ($^1J(CH)$ = 170 Hz) while the other three are due to three inequivalent $=CH_2$ carbons ($^1J(CH) \simeq 150$ Hz). Carbon–carbon bond formation in the reaction leading to 3 and 4 is conclusively demonstrated by the observation of $^{13}C{-}^{13}C$ coupling in the

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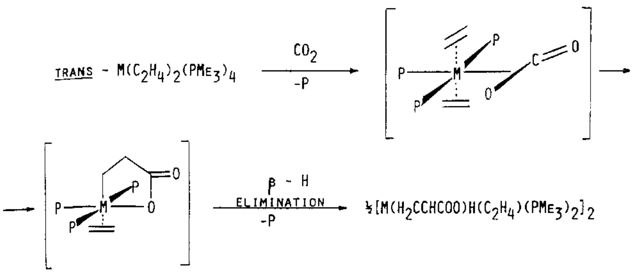
Scheme I



spectrum of 4*: the methynic resonance at 55.1 ppm converts into a singlet and a doublet resembling a ca. 1:2:1 triplet, with a separation of the outer lines, ^1J(CC) = 60 Hz. This coupling is of the same order of magnitude as that of 52 Hz observed between the β-methylene and carbonyl carbons of (η^5-C_5Me_5)$_2$TiO^{13}C(O)^{13}CH$_2$CH$_2$.[6]

Some comments should be devoted at this point to the genesis of the acrylate derivatives 3 and 4, in particular to the C_2H_4–CO_2 coupling mechanism. This problem has been addressed theoretically[7] although no definitive proposal could be made with the available data. There is ample experimental evidence demonstrating the facile dissociation of one of the PMe_3 ligands in compounds 1 and 2 and its substitution by other π-acceptors such as N_2, CO, or CNR to afford *trans,mer*-M(C_2H_4)$_2$(L)(PMe_3)$_3$ complexes.[5b,c,8] It is therefore reasonable to assume that the first step in this transformation is PMe_3 substitution by CO_2, with formation of an intermediate, undetected species, "M(C_2H_4)$_2$(CO_2)(PMe_3)$_3$" (Scheme I). Some conceivable pathways for the CO_2–C_2H_4 coupling are (i) insertion of carbon dioxide into one of the ethylene C–H bonds of the organic fragment followed by hydrogen migration to the metal, (ii) oxidative addition of a vinylic C–H bond of the C_2H_4 ligand to yield an alkenyl hydride and subsequent CO_2 insertion into the resulting M–C bond, and (iii) oxidative coupling of C_2H_4 and CO_2 to afford a five-membered metalla lactone which could undergo β-H elimination to produce the hydrido acrylate structure. Loss of PMe_3 and subsequent dimerization would produce the final complexes 3 and 4. There are precedents in the literature for all of these pathways,[3,4,6,9,10] and although an investigation of the precise coupling mechanism has not been pursued, we would like to point out that both routes (i) and (ii) rely on the assumption of the existence of activated C–H bonds in compounds 1 and 2, an hypothesis for which there is not the slightest experimental evidence. Furthermore, the fact that complex 1 does not react with an excess of Bu^{n}Li (2–3 equiv) in the presence of TMED (TMED = $Me_2NCH_2CH_2NMe_2$) stands against this possibility. It could be argued that CO_2 coordination with the formation of the putative "M(C_2H_4)$_2$(CO_2)(PMe_3)$_3$" could sufficiently modify the electronic structure of the M–C_2H_4 linkage, rendering the olefinic C–H bonds active with respect to this transformation, but this seems also unlikely since the ^{1}H and ^{13}C NMR properties of the ethylene ligands in 1 and 2 are very similar to those found in bis(ethylene) complexes such as M(C_2H_4)$_2$(L)(PMe_3)$_3$, M(C_2H_4)$_2$(L)$_2$(PMe_3)$_2$ (L = CO,[5b,c] CNR[8]), and M(C_2H_4)$_2$(CO)$_4$,[11] which contain one or more π-acid ligands in the plane perpendicular to the C_2H_4–M–C_2H_4 axis. These arguments favor route (iii) (Scheme I), although as already indicated an investigation of the precise coupling mechanism has not been pursued.

Table I. Selected Bond Distances (Å) and Angles (deg) for 3 and 4

	M = Mo, 3 (X-ray)	M = W, 4 (neutron)
	Distances	
M1–P11	2.424 (2)	2.451 (3)
M1–P12	2.424 (2)	2.441 (4)
M1–O1	2.246 (5)	2.221 (3)
M1–O3	2.216 (4)	2.220 (3)
M1–C1	2.220 (6)	2.220 (3)
M1–C2	2.270 (6)	2.242 (3)
M1–C3	2.244 (6)	2.228 (4)
M1–C4	2.209 (6)	2.221 (3)
M1–C5	2.564 (6)	2.532 (3)
M1–Hw1		1.732 (5)
M2–P21	2.425 (2)	2.426 (4)
M2–P22	2.438 (2)	2.441 (4)
M2–O2	2.238 (4)	2.185 (4)
M2–O4	2.229 (5)	2.225 (3)
M2–C6	2.558 (6)	2.540 (3)
M2–C7	2.213 (6)	2.223 (3)
M2–C8	2.238 (6)	2.214 (3)
M2–C9	2.218 (6)	2.220 (3)
M2–C10	2.253 (7)	2.258 (3)
M2–Hw2		1.715 (4)
O1–C5	1.281 (7)	1.303 (2)
O2–C5	1.261 (7)	1.267 (3)
O3–C6	1.268 (7)	1.269 (3)
O4–C6	1.278 (6)	1.309 (3)
C1–C2	1.426 (9)	1.443 (2)
C3–C4	1.418 (8)	1.451 (3)
C4–C5	1.447 (9)	1.454 (2)
C6–C7	1.443 (9)	1.461 (2)
C7–C8	1.423 (2)	1.458 (3)
C9–C10	1.41 (1)	1.462 (2)
	Angles	
P11–M1–O3	155.0 (2)	81.0 (1)
P12–M1–O1	82.9 (1)	85.8 (1)
O1–M1–C3	73.0 (2)	74.0 (1)
O1–M1–C4	61.0 (2)	62.5 (1)
P21–M2–O4	88.5 (1)	88.8 (1)
P21–M2–O2	158.9 (1)	152.2 (1)
O4–M2–C7	61.5 (2)	62.05 (9)
O4–M2–C8	74.0 (2)	73.4 (1)
O1–C5–C4	111.9 (6)	113.2 (2)
O1–C5–O2	121.9 (6)	124.5 (2)
O4–C6–C7	112.8 (5)	111.6 (2)
O3–C6–O4	124.8 (5)	121.5 (2)

Structural Characterization of 3 and 4. X-ray and Neutron Diffraction Studies. The overall molecular configuration of compounds 3 and 4 has been deduced from X-ray studies on both compounds, which show they are isomorphous but not isostructural. Predictibly, the positions of some of the hydrogen atoms were not well-defined, and in particular, a clear distinction between formulation of the compounds as hydride acrylate derivatives or as acrylic acid complexes, with an agostic-type interaction, M–OH, could not be accomplished.[5d] A neutron diffraction study has been performed on the tungsten complex 4, and this has conclusively demonstrated that this compound and, by analogy, 3 are in fact hydride acrylate species containing formally divalent M(II).

For complex 3, the following discussion is based on X-ray data, while for 4 it relies entirely on the results of the neutron diffraction study. X-ray data for 4 are only given

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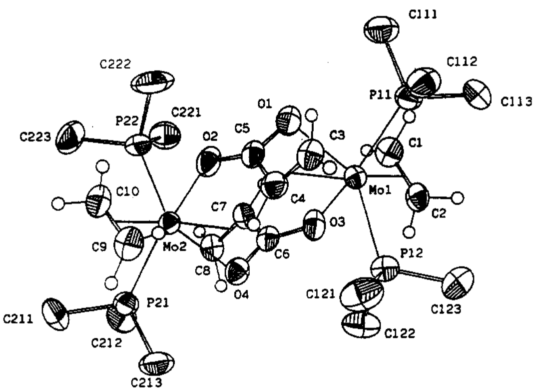

Figure 1. Molecular structure and atom labeling scheme for **3**.

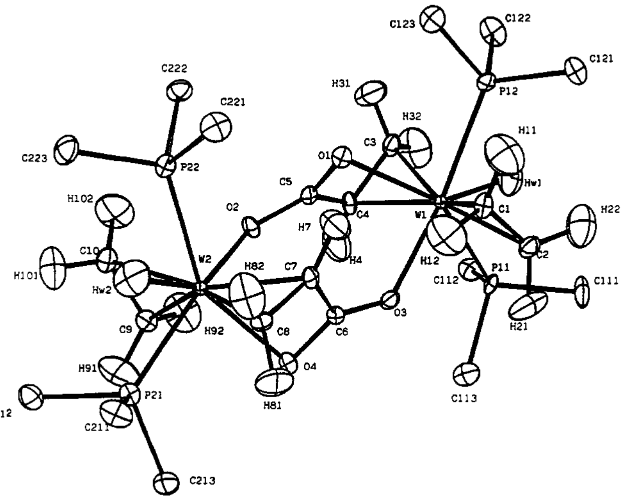

Figure 2. ORTEP diagram and atomic numbering scheme for **4** (neutron diffraction study).

in the supplementary material. Figure 1 shows an ORTEP perspective view of the dimeric molecules of **3**; selected bond distances and angles are given in Table I. The monoclinic crystals of **3** are composed of dimeric molecules that contain two acrylate ligands bridging the two molybdenum centers in a bonding situation somewhat reminiscent of that found in the complex $[Mo(H_2C{=}CHCN)(CO)_2(PBu^n_3)_2]_2$.[12]

The coordination of the olefinic ligands to molybdenum is similar to that found in other related[5b,8,13] complexes and slightly asymmetric (Mo1–C1 = 2.221 (6), Mo1–C2 = 2.270 (6) Å and Mo1–C3 = 2.244 (6), Mo1–C4 = 2.209 (6) Å), but the Mo–C bond lengths are of the same order of magnitude as those found in the parent *trans*-$Mo(C_2H_4)_2(PMe_3)_4$.[5b] The Mo–P bond lengths (2.423 (2) Å, average for Mo1) have normal values and compare well with data reported in the literature for other trimethylphosphine complexes of Mo(II), e.g. $MoH(BH_4)(PMe_3)_4$,[14a] $MoH_2(PMe_3)_5$,[14b] $MoH(OOCH)(PMe_3)_4$.[14b] A more detailed description of the structural characteristics of complexes **3** and **4**, in particular of the metal–acrylate and –ethylene linkages is provided below.

For compound **4**, a low-temperature (20 K) neutron diffraction study has been effected in order to minimize the perturbation due to large thermal motion of the methyl groups of the phosphine ligands. Neutron scattering lengths were taken from Bacon[15] and the refinements performed on F^2 with a weighting scheme, as described in the Experimental Section. Figure 2 shows an ORTEP view of the dimeric molecules of **4**, while Figure 3 displays the coordination geometry around one of the tungsten atoms, W1. Since data for the other tungsten atom are entirely similar, the discussion will be based on data for W1. As can be seen, the coordination polyhedron can be approximately described as a distorted pentagonal bipyramid, with the two olefinic ligands in the axial positions and the two phosphines, the two oxygen atoms (one from each acrylate group), and the hydride ligand in the equatorial plane. The interatomic distances (Table I) within the two acrylate units are identical within experimental error but show some deviations with respect to the corresponding parameters in the free molecule of acrylic acid. In particular, the C3–C4 bond length of 1.451 (3) Å is appreciably longer than the 1.30 Å value found in free acrylic acid.[16] This is likely due to extensive back-donation from the metal center to the C=C bond, and it is in accord with the relatively short W1–C3 and W1–C4 distances of 2.228 (4) and 2.221 (3) Å, respectively. For comparative purposes, W–C bond lengths in the parent *trans*-$W(C_2H_4)_2(PMe_3)_4$ are in the range 2.24–2.27 Å. The C4–C5 bond distance of 1.454 (2) Å is identical, within experimental error, with that found in the butyl methacrylate (vinyl) complex $RuH(CHC(CH_3)COOC_4H_9)(PPh_3)_3$,[17] although in **4** there is a large deviation from planarity as shown by the C3–C4–C5–O2 torsion angle of 153.0 (2)°. The tungsten–ethylene linkage is also characterized by a relatively long C1–C2 bond of 1.443 (2) Å (1.34 Å in free ethylene, 1.42 Å in the parent *trans*-$W(C_2H_4)_2(PMe_3)_4$[5c]) and by essentially symmetrical coordination, W1–C1 and W1–C2 separations of 2.220 (3) and 2.242 (3) Å, respectively. The hydride ligand HW1 is located in the middle of the P11–W1–P12 angle, which opens up to 120.7° so as to better accommodate it. The

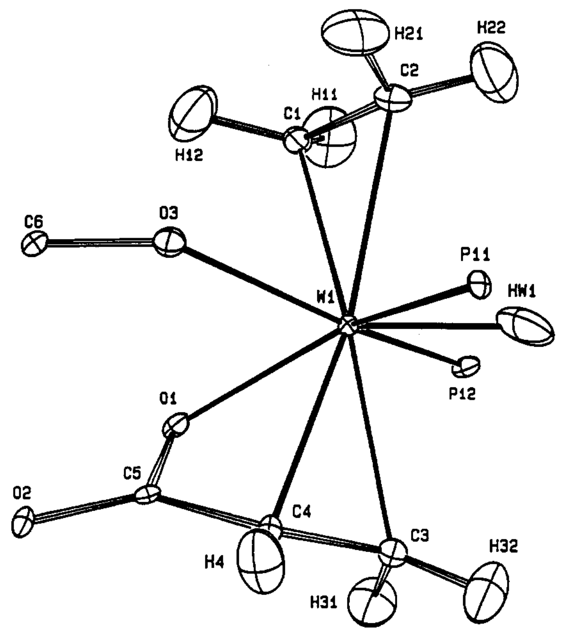

Figure 3. The coordination sphere of W1 in **4**.

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other interatomic angles in the equatorial plane of the distorted pentagonal bipiramid, P11-W1-O3, O3-W1-O1, and O1-W1-P12, have values closed to 80° (see Table I). The W1-HW1 separation of 1.732 (5) Å compares well with distances found by neutron diffraction studies for other tungsten hydride complexes, e.g. 1.65-1.74 Å in the polyhydride $WH_6(PPhPr^i{}_2)_3$.[18] Rather remarkably, this hydride ligand occupies a position that is relatively close to the carbon atoms C2 (2.564 (8) Å) and C3 (2.530 (8) Å), and therefore the geometry of this complex could serve as a model for the transition state or the intermediate of the insertion reaction of a hydride ligand into a metal-olefin bond to afford a σ-alkyl complex. Indeed compounds **3** and **4** can be readily hydrogenated to the corresponding propionate complexes, as discussed below.

Chemical Properties of 3 and 4. Formation of the Propionate Complexes $MoH(OOCCH_2CH_3)(PMe_3)_4$ (5) and $WH_3(OOCCH_2CH_3)(PMe_3)_4$ (6) and the Crystal and Molecular Structure of 6. The reaction leading to the formation of **3** and **4**, starting respectively from **1** and **2** plus CO_2, corresponds formally to an insertion of CO_2 into one of the ethylene C-H bonds[19] (eq 2).

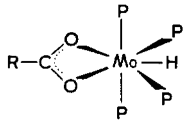
$$H_2C{=}CH_2 + CO_2 \rightarrow H_2C{=}CH{-}COOH \qquad (2)$$

Compounds **1** and **2** can be regenerated from **3** and **4**, respectively, by addition of Bu^nLi under ethylene, in the presence of PMe_3 (eq 3). The white precipitate formed can be readily isolated by filtration and identified as $LiOOCCH{=}CH_2$.

$$\begin{array}{l} \tfrac{1}{2}[\mathrm{MH(OOCCH{=}CH_2)(C_2H_4)(PMe_3)_2}]_2 + 2\mathrm{PMe_3} + \\ \qquad \mathbf{3},\ \mathrm{M = Mo} \\ \qquad \mathbf{4},\ \mathrm{M = W} \\ \qquad\qquad \mathrm{Bu^nLi + C_2H_4} \rightarrow \\ \textit{trans-}\mathrm{M(C_2H_4)_2(PMe_3)_4 + H_2C{=}CHCOOLi + Bu^nH} \\ \qquad \mathbf{1},\ \mathrm{M = Mo} \\ \qquad \mathbf{2},\ \mathrm{M = W} \end{array} \qquad (3)$$

With the aim of liberating acrylic acid from **3** and **4**, their interaction with CO has been investigated. As expected the reactions take place with reductive elimination and formation of a mixture of M(0) carbonyl species $M(CO)_x(PMe_3)_{6-x}$ (x = 4, 5), but we have been unable to trace the liberation of acrylic acid, either by NMR or by GC techniques, even when the reaction was performed in the presence of hydroquinone to inhibit its polymerization.

The acrylate complexes **3** and **4** can be readily hydrogenated, in the presence of PMe_3, to afford the hydrido propionate derivatives **5** and **6**, respectively. For molybdenum the reaction takes place under ambient conditions (20 °C, 1 atm H_2) and furnishes the monohydride $MoH(\eta^2\text{-}OOCCH_2CH_3)(PMe_3)_4$ (**5**), a new representative of a well-known series of hydrido carboxylate complexes described by Wilkinson and co-workers.[14b] Spectroscopic data for **5** are fully in accord with the proposed formulation and indicates structure type B. Similar structures have been advanced previously for related complexes.[14b,20]



B

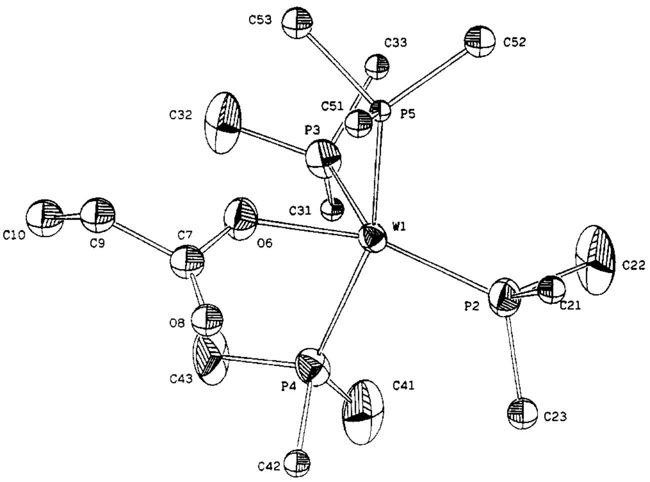


Figure 4. Molecular structure of **6**.

Table II. Bond Distances (Å) and Angles (deg) for 6

Distances			
W1-P2	2.376 (4)	P4-C41	1.86 (3)
W1-P3	2.509 (4)	P4-C42	1.84 (2)
W1-P4	2.43 (1)	P4-C43	1.86 (2)
W1-P5	2.503 (8)	P5-C51	1.88 (2)
W1-O6	2.18 (1)	P5-C52	1.84 (3)
P2-C21	1.85 (2)	P5-C53	1.87 (3)
P2-C22	1.81 (2)	O6-C7	1.38 (2)
P2-C23	1.86 (4)	C7-O8	1.15 (3)
P3-C31	1.89 (3)	C7-C9	1.51 (4)
P3-C32	1.82 (2)	C9-C10	1.35 (4)
P3-C33	1.86 (3)		
Angles			
P2-W1-P3	135.8 (2)	C31-P3-C33	100 (1)
P2-W1-P4	95.9 (2)	C32-P3-C33	100 (1)
P2-W1-P5	95.7 (2)	W1-P4-C41	119.9 (8)
P2-W1-O6	143.4 (3)	W1-P4-C42	119 (1)
P3-W1-P4	92.7 (2)	W1-P4-C43	115 (1)
P3-W1-P5	94.3 (2)	C41-P4-C42	99 (1)
P3-W1-O6	80.8 (3)	C41-P4-C43	101 (1)
P4-W1-P5	154.9 (2)	C42-P4-C43	100 (1)
P4-W1-O6	81.5 (5)	W1-P5-C51	118 (1)
P5-W1-O6	75.9 (5)	W1-P5-C52	121 (1)
W1-P2-C21	119.6 (8)	W1-P5-C53	119 (1)
W1-P2-C22	119.4 (8)	C51-P5-C52	100 (1)
W1-P2-C23	120.2 (9)	C51-P5-C53	96 (1)
C21-P2-C22	98 (1)	C52-P5-C53	98 (1)
C2-P2-C23	97 (1)	W1-O6-C7	131 (1)
C22-P2-C23	98 (1)	O6-C7-O8	126 (2)
W1-P3-C31	116.5 (8)	O6-C7-C9	111 (3)
W1-P3-C32	119.5 (5)	O8-C7-C9	121 (2)
W1-P3-C33	115.7 (7)	C7-C9-C10	119 (4)
C31-P3-C32	102 (1)		

The tungsten acrylate **4** does not react with H_2 under ambient conditions, but conversion into the trihydride species $WH_3(\eta^1\text{-}OOCCH_2CH_3)(PMe_3)_4$ (**6**) can be effected by reaction with 3-4 atm of H_2, in the presence of PMe_3 (20 °C, 10-11 days), under irradiation of a tungsten filament lamp. Three ν(W-H) bands are observed in the IR spectrum of **6** at 1870, 1830, and 1760 cm^{-1}, together with a strong absorption at ca. 1620 cm^{-1} due to the carboxylate ligand. NMR data are in accord with the proposed formulation. They are collected in the Experimental Section and will not be further discussed.

The molecular structure and atom labeling scheme for **6** are presented in Figure 4; selected interatomic distances and angles are provided in Table II. The complex has a distorted dodecahedral geometry, very similar to that

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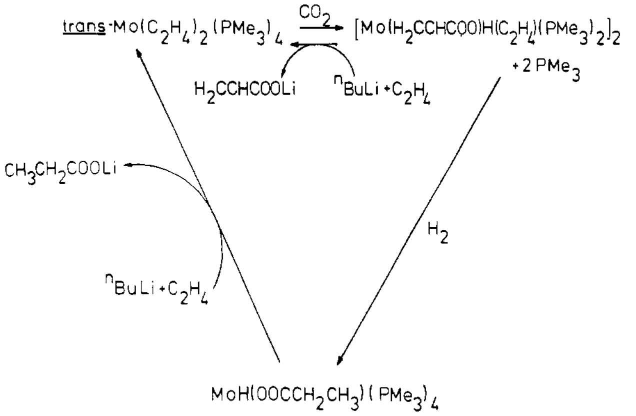
[18] Gregson, D.; Mason, S. A.; Howard, J. A. K.; Spencer, J. L.; Turner, D. G. *Inorg. Chem.* **1984**, *23*, 4103.

[19] Ito, T.; Yamamoto, A. *Organic and Bio-organic Chemistry of Carbon Dioxide*; Inoue, S., Yamazaki, N., Eds.; Wiley: New York, 1982.

[20] Ito, T.; Tosaka, H.; Yoshida, S.; Mita, K.; Yamamoto, A. *Organometallics* **1986**, *5*, 735.

Scheme II



found for the related hydride $WH_3(OPh)(PMe_3)_4$.[21] Not unexpectedly, the W–P bond lengths are not equivalent and span over the relatively wide range of 2.376 (4)–2.509 (4) Å. The shortest of these separations at 2.376 (4) Å corresponds to W–P2, that is, to the phosphine ligand in a transoid position with respect to the carboxylate ligand (O6–W1–P2 angle of 143.4 (3)°). This value is from the short end of the 2.48–2.58 Å range of recently reported values.[22] Similar inequivalences in the W–P separations have been found in $WH_3(OPh)(PMe_3)_4$[21] and $WH_6(PPhPr_2^i)_3$.[18] For the former complex, this shortening has been attributed to an increase of the W→P π bonding induced by the O(2p)→W(3d) π-bonding interaction.[21]

The overall reaction of the formation of a propionate ligand, starting from C_2H_4, CO_2, and H_2, corresponds to ethylene hydrocarboxylation (eq 4), and again the ethylene

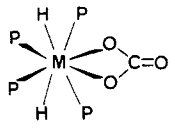
$$H_2C{=}CH_2 + CO_2 + H_2 \rightarrow CH_3CH_2COOH \qquad (4)$$

complexes 1 and 2 can be regenerated starting from 5 and 6, respectively, by reaction with Bu^{n}Li under C_2H_4, therefore making the process cyclic as depicted in Scheme II for the molybdenum system.

Since the propionate complexes 5 and 6 are obtained in a two-step reaction, starting from 1 and 2, respectively, an attempt has been made to carry out their synthesis by the direct reaction of 1 or 2 with a 1:1 mixture of CO_2 and H_2. This reaction takes a different course, as discussed below.

The stirring of THF solutions of the ethylene complexes 1 and 2 with a 1:1 mixture of CO_2/H_2 (30–40 h, 20 °C, ca. 4 atm total pressure) produces the hydrido carbonate species $MH_2(CO_3)(PMe_3)_4$ (M = Mo, 7; M = W, 8). Both compounds are yellow crystalline materials, sparingly soluble in hydrocarbon and ether solvents but more soluble in Cl_2CH_2. Although moderately stable in the solid state, they decompose in solution in contact with air. Their IR spectra display two medium-intensity M–H stretches in the proximity of 1800 cm^{-1} and a strong absorption around 1620 cm^{-1} which can be assigned to a bidentate carbonate ligand.[23] Further evidence for the presence of the carbonate group comes from the appearance of a ^{13}C NMR signal at ca. 165 ppm in the $^{13}C\{^1H\}$ NMR spectrum of 7 and 8. The relatively low solubility of the compounds, the long relaxation time of the ^{13}C nucleus of the CO_3^{2-} group, and its coupling to the ^{31}P nuclei make observation of this signal difficult, but for 7 a triplet can be observed due to coupling to two equivalent ^{31}P nuclei (^2J(CP) = 10 Hz).

While our work was in progress, a related dmpe complex, $MoH_2(CO_3)(dmpe)_2$ (dmpe = $Me_2PCH_2CH_2PMe_2$), exhibiting similar NMR properties has been reported.[24] The tungsten complex 8 has also been prepared during the course of this work, but no spectroscopic data have been provided.[25] Simulation of the ^1H (hydride region) and $^{31}P\{^1H\}$ NMR spectra leads to the NMR parameters detailed in the Experimental Section, which are fully in accord with the proposed structure C.



C

The formation of carbonato complexes from the reactions of CO_2 with transition-metal compounds is well-documented in the literature,[24-27] and therefore a detailed investigation of this transformation has not been attempted. Some comments can however be made on the basis of the available data, which can be summarized as follows: (i) 7 and 8 are not formed when 1 or 2 are reacted with CO_2 and H_2O, in the absence of hydrogen; this demonstrates the participation of H_2 in this reaction, possibly by formation of the hydrides $MH_4(PMe_3)_4$ (or related polyhydride species). (ii) Carboxylation of $MoH_4(PMe_3)_4$[14b] produces a mixture of $MoH_2(CO_3)(PMe_3)_4$ and $MoH(OOCH)(PMe_3)_4$. The latter is the only product of the reaction of $MoH_2(PMe_3)_5$ and CO_2[21] and is also present in the reaction mixture leading to 7. (iii) The reaction of 2 with a 1:1 mixture of CO_2/D_2, in the presence of H_2O, affords only $WD_2(CO_3)(PMe_3)_4$, while a mixture of CO_2 and H_2, plus D_2O, yields $WH_2(CO_3)(PMe_3)_4$. Taken together, these observations are consistent (but do not prove) with the formation of the carbonates 7 and 8 by protonation of the corresponding polyhydrides (e.g. $MH_4(PMe_3)_4$) by H_2CO_3, possibly through the intermediacy of the hydride bicarbonate species.

Reactions of CO_2 with Other Related Complexes. In order to gain additional information on the reactions leading to the acrylate complexes 3 and 4, we have attempted promoting this transformation by closely related transition-metal systems.

We have been unable to obtain bis(ethylene) complexes of molybdenum containing the bulky PPr_3^i and PCy_3 phosphine ligands, either by PMe_3 substitution in 1 or by reduction of $MoCl_3(THF)_3$ under C_2H_4 in the presence of PR_3. PMe_3 substitution in 1 and 2 by the π-acid CO or CNR ligands can be accomplished[8] with formation of mono- and disubstituted products $M(C_2H_4)_2(L)_n(PMe)_{4-n}$ (n = 1, 2), but these compounds do not seem to react with CO_2. With the aim of preparing bis(propylene) complexes analogous to 1 and 2, the reduction of $MCl_4(PMe_3)_3$[28] with Na–Hg, under propylene, was effected (eq 5). The hydrido

$$MCl_4(PMe_3)_3 \xrightarrow[PMe_3]{Na\text{-}Hg,\ C_3H_6} \begin{array}{l} MH(\eta^3\text{-}C_3H_5)(PMe_3)_4 \\ \mathbf{9},\ M = Mo \\ \mathbf{10},\ M = W \end{array} \qquad (5)$$

allyls 9 and 10 were instead obtained. These compounds

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[21] Chiu, K. W.; Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthose, M. B.; Abdul Malik, K. M. *J. Chem. Soc. Dalton Trans.* **1981**, 1204.

[22] See ref 13 of ref 18.

[23] See: Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds.*, 3rd ed.; Wiley: New York, 1978.

[24] Fong, L. K.; Fox, J. R.; Cooper, N. J. *J. Am. Chem. Soc.* **1987**, *6*, 223.

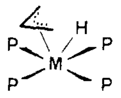
[25] Green, M. L. H.; Parkin, G. *J. Chem. Soc., Chem. Commun.* **1986**, 90.

[26] See, for example: (a) Krogsrud, S.; Komiya, S.; Ito, T.; Ibers, J. A.; Yamamoto, A. *Inorg. Chem.* **1976**, *15*, 2798. (b) Lundquist, E. G.; Folting, K.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1987**, *26*, 205.

[27] Palmer, D. A.; van Eldik, R. *Chem. Rev.* **1983**, *83*, 651.

[28] Carmona, E.; Galindo, A.; Rogers, R. D.; Atwood, J. L.; Canada, L. G. *J. Organomet. Chem.* **1984**, *277*, 403.

are formed as yellow-brown oils, which convert into yellow powders by action of vacuum. The high solubility they display in the organic solvents in which they do not decompose has precluded their isolation in a pure crystalline form. Nevertheless, spectroscopic data are fully in accord with the proposed formulation and are in agreement with data reported for the analogous dppe complex $\mathrm{MoH}(\eta^3\text{-}\mathrm{C_3H_5})(\mathrm{dppe})_2$ (dppe = $\mathrm{Ph_2PCH_2CH_2PPh_2}$) for which a structure of type D has been proposed.[13] Compounds **9** and **10** are fluxional and exhibit a singlet in the fully ^{1}H-decoupled, room-temperature, ^{31}P NMR spectrum, which converts into a doublet when selectively decoupling the $\mathrm{PMe_3}$ protons. The hydride ligand gives rise to an IR band around 1700 cm^{-1} and to a quintet in the high-field region of the ^{1}H NMR spectrum (ca. δ −4.5 ($^2J(\mathrm{HP})$ = 50 Hz)). Other pertinent NMR data are compiled in the Experimental Section and require no further comment. Despite the failure to isolate the desired η^2-propylene complexes, the reactivity of **9** and **10** was tested. In addition to reactions with CO, $\mathrm{H_2}$, and $\mathrm{C_2H_4}$, which are described in the Experimental Section, interaction with $\mathrm{CO_2}$ yields propylene and the known compounds *trans*-$\mathrm{Mo(CO_2)_2(PMe_3)_4}$[5c] and $\mathrm{Mo(CO_3)(CO)(PMe_3)_4}$[29] for complex **9** and $\mathrm{W(CO_3)(CO)(PMe_3)_4}$[30] plus $\mathrm{WH_2(CO_3)(PMe_3)_4}$ for the tungsten analogue.



D

Experimental Section

Microanalyses were by Pascher Microanalytical Laboratory, Bonn. Molecular weights were measured cryoscopically in benzene, under nitrogen. Infrared spectra were recorded on Perkin-Elmer spectrophotometers, Models 577 and 684. ^{1}H, ^{13}C, and ^{31}P NMR spectra were run on a Varian XL-200 spectrometer. ^{31}P shifts were measured with respect to external 85% $\mathrm{H_3PO_4}$. ^{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 $\mathrm{SiMe_4}$. 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 of 40–60 °C. The compounds *trans*-$\mathrm{M(C_2H_4)_2(PMe_3)_4}$ (M = Mo, W) were prepared according to the literature procedures.[5b,c] The $\mathrm{PMe_3}$ ligand was obtained by the method of Wolfsberger and Schmidbaur.[31]

Synthesis of $\mathbf{[MoH(OOCCHCH_2)(C_2H_4)(PMe_3)_2]_2}$ (3). Complex **1** (0.6 g, ca. 1.3 mmol) was dissolved in 60 mL of $\mathrm{Et_2O}$, and $\mathrm{CO_2}$ was bubbled through this solution at −20 °C for 20 min. The resulting precipitate was filtered off at low temperature and dried in vacuo. A finely divided solid was obtained that was washed with 2 × 5 mL of petroleum ether and dried in vacuo. From the mother liquor an additional crop of crystals of the title compound was obtained by concentration of the solution under vacuum and cooling at −40 °C overnight. The two solid fractions were recrystallized from large volumes of $\mathrm{Et_2O}$ to provide moderate yields of **3** (ca. 0.14 g, 30%). Selected analytical and spectroscopic data for **3** are as follows: IR (Nujol mull, cm^{-1}) 3030 m, 1790 m, 1510 s, 1160 s, 945 s, 850 m, 790 s, 720 s, 660 s, 450 m, 410 m (representative absorptions); ^{1}H NMR (200 MHz, $\mathrm{C_6D_6}$) δ −6.07 (ddt, 1 H, Mo–*H*, $^2J(\mathrm{HP_A})$ = 105.0, $^2J(\mathrm{HP_B})$ = 98.9, $^3J(\mathrm{HH})$ = 2.3 Hz), 0.87 (d, 9 H, $\mathrm{P(C}H_3)_3$, $^2J(\mathrm{HP})$ = 8.3 Hz), 1.06 (d, 9 H, $\mathrm{P(C}H_3)_3$, $^2J(\mathrm{HP})$ = 8.7 Hz), 1.36 (ddd, 1 H, $H_\mathrm{A}\mathrm{H_BC{=}CH_C{-}COO}$, $^3J(\mathrm{H_AP})$ = 18.5, $^3J(\mathrm{H_AH_C})$ = 7.0, $^2J(\mathrm{H_AH_B})$ = 2.6 Hz), 1.89 (m, 2 H, $H_2\mathrm{C{=}CH_2}$), 2.12 (m, 1 H, $\mathrm{H_A}H_\mathrm{B}\mathrm{C{=}CH_C{-}COO}$), 2.56 (m, 2 H, $\mathrm{H_2C{=}C}H_2$), 3.99 (pseudoquartet, 1 H, $\mathrm{H_AH_BC{=}C}H_\mathrm{C}\mathrm{{-}COO}$, $^3J(\mathrm{H_CH_A}) \simeq {}^3J(\mathrm{H_CH_B}) \simeq {}^3J(\mathrm{H_CP})$ = 7 Hz); ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$) δ 29.6 (d, 1 $\mathrm{P_1}$, $^2J(\mathrm{P_1P_2})$ = 57 Hz), 34.4 (d, 1 $\mathrm{P_2}$); ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$) δ 15.7 (d, 1 $\mathrm{P(}C\mathrm{H_3)_3}$, $^1J(\mathrm{CP})$ = 30 Hz), 18.2 (d, 1 $\mathrm{P(}C\mathrm{H_3)_3}$, $^1J(\mathrm{CP})$ = 29 Hz), 41.9 (dd, $\mathrm{H_2}C\mathrm{{=}CH_2}$, $^2J(\mathrm{CP_A})$ = 9.5, $^2J(\mathrm{CP_X})$ = 2.4 Hz), 46.9 (dd, $\mathrm{H_2C{=}}C\mathrm{H_2}$, $^2J(\mathrm{CP_A})$ = 11.7, $^2J(\mathrm{CP_X})$ = 4.1 Hz), 47.3 (d, $\mathrm{H_2}C\mathrm{{=}CH{-}COO}$, $^2J(\mathrm{CP})$ = 5.9 Hz), 61.5 (d, $\mathrm{H_2C{=}}C\mathrm{H{-}COO}$, $^2J(\mathrm{CP})$ = 3.5 Hz), 179.4 (br, $\mathrm{H_2C{=}CH{-}}C\mathrm{OO}$). Anal. Calcd for $\mathrm{[MoH(OOCCHCH_2)(C_2H_4)(PMe_3)_2]_2}$: C, 37.9; H, 7.5. Found: C, 37.2; H, 7.4.

Synthesis of $\mathbf{[WH(OOCCHCH_2)(C_2H_4)(PMe_3)_2]_2}$ (4). Complex **2** (0.96 g, ca. 1.75 mmol), dissolved in 80 mL of $\mathrm{Et_2O}$, was reacted with $\mathrm{CO_2}$ (20 °C, 1 atm) for 30 min. During this time **4** normally precipitates as a white crystalline material and it is separated by filtration. The supernatant solution was cooled at −20 °C overnight. A total of 0.5 g (ca. 65%) of white crystals of **4** were collected from this and subsequent crystallizations of the mother liquor. A sample of **4**, approximately 50% enriched in $^{13}\mathrm{CO_2}$, **4***, was obtained by the same procedure using $^{13}\mathrm{CO_2}$ (50%) obtained from a 1:1 mixture of $\mathrm{Ba^{13}CO_3}$ and $\mathrm{BaCO_3}$ by addition of concentrated $\mathrm{H_2SO_4}$. Selected analytical and spectroscopic data for **4** are as follows: IR (Nujol mull, cm^{-1}) 3020 w, 1830 w, 1510 s, 1410 m, 1350 w, 1325 w, 1295 m, 1275 s, 1160 w, 1130 s, 1100 w, 1040 w, 945 s, 850 w, 785 m, 760 w, 720 m, 710 m, 660 m, 470 w, 360 m; IR (KBr pellet, $\mathrm{CO_2}$ absorptions, cm^{-1}) 1510 s, 1350 w, 1295 m, 785 m (**4*** displays $^{13}\mathrm{CO_2}$ absorptions at 1480 s, 1310 w, 1250 w, 760 m cm^{-1}); ^{1}H NMR (200 MHz, $\mathrm{C_6D_6}$) δ −1.06 (ddt, 1 H, W–*H*, $^2J(\mathrm{HP_A})$ = 97.7, $^2J(\mathrm{HP_X})$ = 90.4, $^3J(\mathrm{HH})$ = 8 Hz), 0.96 (d, 9 H, $\mathrm{P(C}H_3)_3$, $^2J(\mathrm{HP})$ = 8.6 Hz), 1.13 (d, 9 H, $\mathrm{P(C}H_3)_3$, $^2J(\mathrm{HP})$ = 8.6 Hz), 1.44 (dt, 1 H, $H_\mathrm{A}\mathrm{H_BC{=}CH_C{-}COO}$, $^3J(\mathrm{H_AP})$ = 21.6, $^3J(\mathrm{H_AH_B}) \simeq {}^3J(\mathrm{H_AH_C})$ = 5 Hz), 1.62 (m, 1 H, $H\mathrm{HC{=}CH_2}$), 1.76 (m, 1 H, $\mathrm{H_2C{=}CH}H$), 1.93 (m, 2 H, $\mathrm{H}H\mathrm{C{=}CH_2}$ and $\mathrm{H}H\mathrm{C{=}CH{-}COO}$), 2.10 (m, 1 H, $\mathrm{H_2C{=}C}H\mathrm{H}$), 3.77 (pseudoquartet, 1 H, $\mathrm{H_2C{=}C}H\mathrm{{-}COO}$, $^3J(\mathrm{H_CH_A}) \simeq {}^3J(\mathrm{H_CH_B}) \simeq {}^3J(\mathrm{H_CP})$ = 7 Hz); ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$) δ 0.6 (d, 1 $\mathrm{P_1}$, $^2J(\mathrm{P_1P_2})$ = 58, $^1J(\mathrm{P_1W})$ = 177 Hz, in the spectrum of **4*** (50% enriched in $^{13}\mathrm{CO_2}$) each line of the doublet appears as a singlet plus a doublet with $^3J(\mathrm{P_1C})$ = 2.6 Hz), 9.3 (d, 1 $\mathrm{P_2}$, $^1J(\mathrm{P_2W})$ = 204 Hz); ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$) δ 14.5 (d, 1 $\mathrm{P(}C\mathrm{H_3)_3}$, $^1J(\mathrm{CP})$ = 34 Hz), 17.2 (d, 1 $\mathrm{P(}C\mathrm{H_3)_3}$, $^1J(\mathrm{CP})$ = 33 Hz), 32.8 (dd, $\mathrm{H_2}C\mathrm{{=}CH_2}$, $^2J(\mathrm{CP_A})$ = 10.9, $^2J(\mathrm{CP_X})$ = 2 Hz), 38.3 (dd, $\mathrm{H_2C{=}}C\mathrm{H_2}$, $^2J(\mathrm{CP_A})$ = 13, $^2J(\mathrm{CP_X})$ = 2.8 Hz), 39.6 (d, $\mathrm{H_2}C\mathrm{{=}CH{-}COO}$, $^2J(\mathrm{CP})$ = 6 Hz), 55.1 (d, $\mathrm{H_2C{=}}C\mathrm{H{-}COO}$, $^2J(\mathrm{CP})$ = 3 Hz, this signal becomes a 1:2:1 pseudotriplet in the spectrum of **4*** with $^1J(\mathrm{CC})$ = 60 Hz), 175.5 (d, $\mathrm{H_2C{=}CH{-}}C\mathrm{OO}$, $^3J(\mathrm{CP})$ = 4.7 Hz); M_w (cryoscopically, $\mathrm{C_6H_6}$, $\mathrm{N_2}$, $\mathrm{Et_2O}$-free sample) calcd for $\mathrm{[WH(OOCCHCH_2)(C_2H_4)(PMe_3)_2]_2}$ 872, found 822. Anal. Calcd for $\mathrm{[WH(OOCCHCH_2)(C_2H_4)(PMe_3)_2]_2\cdot{}^1/_2Et_2O}$: C, 31.7; H, 6.3. Found: C, 31.6; H, 6.3.

Reactions of 3 and 4. (a) With $\mathbf{Bu^nLi}$ and $\mathbf{PMe_3}$ under $\mathbf{C_2H_4}$. To a solution of **4** (0.47 g, 0.5 mmol) in 20 mL of $\mathrm{C_6H_6}$, under an atmosphere of ethylene was added successively $\mathrm{PMe_3}$ (0.4 mL, ca. 4 mmol, an excess) and $\mathrm{Bu^nLi}$ (2 mL of a ca. 0.9 M solution in hexane). After this mixture was stirred at room temperature for 40–50 min, the solvent was removed in vacuo and the residue was extracted with petroleum ether (3 × 12 mL) and centrifuged. A white solid, insoluble in petroleum ether, was obtained, and it was identified as lithium acrylate, $\mathrm{LiOOCCH{=}CH_2}$, by comparison of its IR and ^{1}H NMR with those of an authentic sample. The supernatant solution was shown to contain **2** by ^{31}P{^{1}H} NMR spectroscopy, and it was converted into *trans,mer*-$\mathrm{W(C_2H_4)_2(CO)(PMe_3)_3}$ by reaction with CO. The analogous molybdenum complex **3** shows similar reactivity.

(b) With CO. A portion of complex **3** or **4** (ca. 1 mmol) was dissolved in a mixture of $\mathrm{Et_2O}$ (30 mL) and THF (20 mL) and treated with $\mathrm{PMe_3}$ (0.6 mL, an excess). The solution was pressurized with 2 atm of CO and stirred at room temperature for 40 h (**4** requires longer reaction times, ca. 3–4 days, and irradiation with a tungsten filament lamp). The originally colorless solution became yellow, and very small amounts of an unidentified microcrystalline precipitate were gradually formed. The solution was shown spectroscopically, IR and ^{31}P{^{1}H} NMR, to contain a mixture of the carbonyl compounds[32] $\mathrm{M(CO)}_x\mathrm{(PMe_3)}_{6-x}$ (x = 2–5; M = Mo, W). Acrylic acid was not, however, detected either

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spectroscopically or by GC techniques. In the absence of added PMe_3 the reaction takes a similar course, but the resulting carbonyls are $M(CO)_4(PMe_3)_2$ and $M(CO)_5(PMe_3)$ (M = Mo, W).

(c) With Hydrogen and PMe_3: Synthesis of $MoH(OOCCH_2CH_3)(PMe_3)_4$ (5) and $WH_3(OOCCH_2CH_3)(PMe_3)_4$ (6). Complex **3** (0.35 g, 0.5 mmol) was dissolved in 25 mL of THF, and PMe_3 (0.3 mL, ca. 3 mmol) was added. The solution was reacted with H_2 (1 atm) by stirring at room temperature over a period of ca. 8 h and then evaporated to dryness. The residue was extracted with petroleum ether to give a red solution. Centrifugation, partial evaporation of the solvent, and cooling at −20 °C overnight afforded **5** as red crystals (75% yield). IR (Nujol mull, selected absorptions, cm^{-1}): 1725 m, 1540 s, 1295 s, 1275 s, 935 s, 890 s, 850 s, 700 s, 650 s. ^1H NMR (200 MHz, C_6D_6): δ −8.42 (tt, 1 H, Mo–H, $^2J(HP_A)$ = 86.9, $^2J(HP_X)$ = 11.3 Hz), 1.21 (t, 18 H, 2 $P(CH_3)_3$, J_{app} = 4 Hz), 1.20 (t, 3 H, CH_3CH_2–, partially obscured by PMe_3 absorptions), 1.49 (doublet with central intensity, 18 H, 2 $P(CH_3)_3$, J_{app} = 3.6 Hz), 2.24 (q, 2 H, CH_3CH_2–, $^3J(HH)$ = 7.3 Hz); $^{31}P\{^1H\}$ NMR (C_6D_6) A_2X_2 spin system, δ 5.8 (t, 2 PMe_3, $^2J(P_AP_X)$ = 21 Hz), 38.6 (t, 2 PMe_3); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 9.7 (s, CH_3), 20.9 (t, 2 $P(CH_3)_3$, J_{app} = 6.6 Hz), 27.5 (pseudotriplet, 2 $P(CH_3)_3$, J_{app} = 11.1 Hz), 30.8 (s, CH_2), 178.1 (br, COO). Anal. Calcd for $MoH(OOCCH_2CH_3)(PMe_3)_4$: C, 38.0; H, 8.9. Found: C, 38.2; H, 8.9.

The tungsten acrylate complex **4** was reacted with H_2 in a similar manner: onto a solution of **4** (1.2 g, 1.3 mmol) in 30 mL of THF was added an excess of PMe_3 (0.9 mL). The mixture was pressurized with H_2 (4 atm) and stirred at room temperature for 10–11 days under irradiation (tungsten filament lamp). Small amounts of an unidentified yellow microcrystalline solid and a yellow-orange solution were obtained. The solution was centrifuged and the solvent removed under vacuum. The residue was extracted with petroleum ether (2 × 20 mL) and centrifuged again. Concentration and cooling at −30 °C afforded **6** as white yellowish needles. From this crop and from subsequent crystallizations of the mother liquor 1 g of **6** (ca. 70% yield) was obtained: IR (KBr pellet, cm^{-1}) 2970 m, 2910 m, 1870 m, 1830 m, 1760 m, 1620 s, 1420 m, 1370 m, 1290 m, 1280 m, 1270 m, 1240 m, 1070 m, 940 s, 850 s, 720 s, 705 s, 610 m; ^1H NMR (200 MHz, C_6D_6) δ −3.29 (simetric multiplet, 3 H, W–H), 1.30 (d, 9 H, 1 $P(CH_3)_3$, $^2J(HP)$ = 6.6 Hz), 1.35 (t, 3 H, CH_3CH_2–, $^3J(HH)$ = 6.6 Hz), 1.41 (t, 18 H, 2 $P(CH_3)_3$, J_{app} = 3.1 Hz), 1.46 (d, 9 H, 1 $P(CH_3)_3$, $^2J(HP)$ = 7.9 Hz), 2.33 (q, 2 H, CH_3CH_2–); $^{31}P\{^1H\}$ NMR (C_6D_6) AMNX spin system, δ −22.6 (dd, P_X, $^2J(P_XP_A)$ = 57, $^2J(P_XP_M)$ = 18.5, $^1J(P_XW)$ = 151 Hz), −20.3 (d, P_N, $^2J(P_NP_A)$ = 17, $^1J(P_NW)$ = 125 Hz), −20.0 (d, P_M, $^1J(P_MW)$ = 125 Hz), −12.2 (dd, P_A, $^1J(P_AW)$ = 135 Hz); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 11.5 (s, CH_3), 23.3 (t, 2 $P(CH_3)_3$, J_{app} = 12 Hz), 23.6 (d, 1 $P(CH_3)_3$, $^1J(CP)$ = 19.8 Hz), 31.4 (s, CH_2), 31.5 (d, 1 $P(CH_3)_3$, $^1J(CP)$ = 31.6 Hz), 176.4 (br, COO). Anal. Calcd for $WH_3(OOCCH_2CH_3)(PMe_3)_4$: C, 31.9; H, 7.8. Found: C, 32.2; H, 7.9.

Reaction of 5 with Bu^nLi under C_2H_4. Bu^nLi (0.78 mL, solution 0.9 M in hexane) was added to a solution of **5** (0.24 g, ca. 0.5 mmol) in 30 mL of petroleum ether at −20 °C, under an atmosphere of C_2H_4. The mixture was stirred and warmed slowly until room temperature. The color changed from red to orange-yellow, and a white solid precipitated. After 30–40 min the suspension was centrifuged and the white solid washed with Et_2O (2 × 5 mL) and dried in vacuo. It was identified spectroscopically as lithium propionate, $LiOOCCH_2CH_3$, while the solution was shown to contain **1**, which was isolated by crystallization from petroleum ether.

Synthesis of $MH_2(CO_3)(PMe_3)_4$ (M = Mo, 7; M = W, 8) Complexes. A solution of *trans*-$M(C_2H_4)_2(PMe_3)_4$ (ca. 1 mmol) in THF (50 mL) was pressurized with a 1:1 mixture of CO_2 and H_2 to a total pressure of 4 atm and stirred at room temperature for 30–40 h. A yellow solid was formed and separated by centrifugation, washed with Et_2O (2 × 10 mL), and dried in vacuo. **7** (0.21 g, ca. 30%) or 0.3 g of **8** (ca. 36%) was thus obtained. Analytically pure, yellow crystals of both compounds were obtained by crystallization from small volumes of Cl_2CH_2. The deuterated compound $WD_2(CO_3)(PMe_3)_4$ (**8***) was obtained similarly by using a CO_2/D_2 mixture (1:1). Analytical and spectroscopic data for **7**: IR (Nujol mull, cm^{-1}) 1845 m, 1605 s, 1430 m, 1300 m, 1285 m, 1275 m, 1235 m, 1015 m, 950 s, 860 m, 830 m, 800 w, 730 m, 670 m; ^1H (200 MHz, Cl_2CD_2) δ −4.49 (ddt, 2 H, Mo–H, $^2J(HP_A)$ = 55, $^2J(HP_X)$ = 45, $^2J(HP_Y)$ = 40 Hz), 1.28 (t, 18 H, 2 $P(CH_3)_3$, J_{app} = 3 Hz), 1.44 (doublet with central intensity, 18 H, 2 $P(CH_3)_3$, J_{app} = 3.6 Hz); $^{31}P\{^1H\}$ NMR (Cl_2CD_2) δ −24.1 (t, 2 PMe_3, $^2J(PP)$ = 17.5 Hz), 1.7 (t, 2 PMe_3); $^{13}C\{^1H\}$ NMR (Cl_2CD_2) δ 17.4 (t, 2 $P(CH_3)_3$, J_{app} = 10 Hz), 23.8 (pseudotriplet, 2 $P(CH_3)_3$, J_{app} = 13.4 Hz), 164.6 (t, CO_3, $^2J(CP)$ = 10 Hz). Anal. Calcd for $MoH_2(CO_3)(PMe_3)_4$: C, 33.8; H, 8.2; O, 10.4. Found: C, 33.6; H, 8.4; O, 11.1. Analytical and spectroscopic data for **8**: IR (Nujol mull, cm^{-1}) 1895 m, 1855 m, 1620 s, 1435 m, 1300 m, 1285 m, 1280 sh, 1240 m, 1020 m, 955 s, 875 m, 860 m, 750 m, 730 m, 720 m, 670 m; ^1H (200 MHz, Cl_2CD_2) δ −1.73 (ddt, 2 H, W–H, $^2J(HP_A)$ = 47, $^2J(HP_X)$ = 40, $^2J(HP_Y)$ = 37 Hz), 1.39 (t, 18 H, 2 $P(CH_3)_3$, J_{app} = 3 Hz), 1.57 (doublet with central intensity, 18 H, 2 $P(CH_3)_3$, J_{app} = 4 Hz); $^{31}P\{^1H\}$ NMR (Cl_2CD_2) δ −9.1 (t, 2 PMe_3, $^2J(PP)$ = 8.5, $^1J(PW)$ = 217 Hz), −16.1 (t, 2 PMe_3, $^1J(PW)$ = 211 Hz); $^{13}C\{^1H\}$ NMR (Cl_2CD_2) δ 17.9 (t, 2 $P(CH_3)_3$, J_{app} = 12 Hz), 24.9 (pseudotriplet, 2 $P(CH_3)_3$, J_{app} = 8 Hz), 164.0 (br, CO_3). Anal. Calcd for $WH_2(CO_3)(PMe_3)_4$: C, 28.4; H, 6.9. Found: C, 28.2; H, 6.9.

Reaction of 8 with HCl. Over a solution of **8** (0.25 g, 0.51 mmol) in MeOH (8 mL) was added 2 equiv of $ClSiMe_3$ (ca. 0.14 mL) via syringe. The solution was stirred for 30 min and the solvent stripped off in vacuo. The yellow residue was quantitatively constituted by $WH_2Cl_2(PMe_3)_4$, which was identified spectroscopically (IR, NMR) by comparison with the data previously reported.[33] In this reaction 1 mol of CO_2 was evolved per mole of complex (measured by Toepler pump techniques and identified by GC).

Synthesis of $MH(\eta^3\text{-}C_3H_5)(PMe_3)_4$ (M = Mo, 9; M = W, 10) Complexes. To a suspension of 0.9 g of amalgamated (1%) sodium, in propylene-saturated THF (80 mL), was added 6 mmol of $MCl_4(PMe_3)_3$ (M = Mo, 2.8 g; W, 3.3 g). The mixture was stirred at room temperature under an atmosphere of propylene until all the $MCl_4(PMe_3)_3$ had been taken into solution, and the color changed to brown yellowish. After approximately 30–40 min of stirring, 0.5 mL (ca. 5 mmol) of PMe_3 was added and the mixture further stirred at room temperature for an additional 4–5 h. The suspension was then centrifuged, the solution evaporated to dryness, and the residue extracted with petroleum ether (45 mL) and cooled to −30 °C overnight, to precipitate most of the $MCl_2(PMe_3)_4$ formed. The solvent was removed in vacuo to produce a yellow brownish oil, which converted into a solid after being pumped for a few minutes under vacuum. Complexes **9** and **10** are obtained as yellow powders in yields of 52% (M = Mo) and 48% (M = W) (referred to PMe_3). Spectroscopic data for **9**: IR (Nujol mull, cm^{-1}) 1700 m (Mo–H); ^1H NMR (200 MHz, C_6D_6) δ −4.68 (quintet, 1 H, Mo–H, $^2J(HP)$ = 51 Hz), 1.16 (br s, 36 H, 4 $P(CH_3)_3$), 1.3 (d, 2 H, CH_2), 3.86 (m, 2 H, CH_2), 4.36 (quintet, 1 H, CH, $^3J(HH)$ = 6.6 Hz); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 7.67 (s, 4 PMe_3); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 25.6 (br s, 4 $P(CH_3)_3$), 35.0 (quintet, CH_2, $^2J(CP)$ = 4 Hz), 81.4 (s, CH). Spectroscopic data for **10**: IR (Nujol mull, cm^{-1}) 1730 m (W–H); ^1H NMR (200 MHz, C_6D_6) δ −4.21 (quintet, 1 H, W–H, $^2J(HP)$ = 46 Hz), 1.29 (pseudotriplet, 36 H, 4 $P(CH_3)_3$, J_{app} = 2.8 Hz), 2.0 (d, 2 H, CH_2), 3.3 (m, 2 H, CH_2), 4.0 (m, 1 H, CH); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −30.78 (s, 4 PMe_3, $^1J(PW)$ = 264 Hz); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 26.0 (br s, 4 $P(CH_3)_3$), 27.2 (quintet, CH_2, $^2J(CP)$ = 4 Hz), 72.1 (s, CH).

Reactions of 9 and 10 with Carbon Dioxide. A solution of 1 mmol of $MH(\eta^3\text{-}C_3H_5)(PMe_3)_4$ (M = Mo, 0.44 g; M = W, 0.53 g) in 20 mL of THF was pressurized with 3 atm of CO_2. The mixture was stirred for 20 h at room temperature and then centrifuged. The dark blue precipitate was identified spectroscopically as $M(CO_3)(CO)(PMe_3)_4$ (M = Mo,[29] W[30]). The supernatant solution was concentrated in vacuo and cooled at −30 °C overnight. For M = Mo, an orange microcrystalline product identified as a mixture of *trans*-$Mo(CO_2)(PMe_3)_4$[5a] and $[Mo(CO_3)(CO)(PMe_3)_3]_2$[29] was obtained, while for tungsten, the yellow microcrystalline solid collected was identified as **8**.

Reaction of 9 with H_2, with C_2H_4, and with CO. For all these reactants a solution of 0.44 g of **9** (1 mmol) in 20 mL of Et_2O was pressurized with 3–4 atm of the gas (H_2, C_2H_4, or CO). The reactions afforded respectively $MoH_4(PMe_3)_4$[34] (55% yield), 1

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Table III. Summary of Crystal, Data Collection and Refinement Parameters for 3, 4, and 6

	3	4 (X-ray)	4 (neutron)	6
		(a) Crystal Data		
formula	$C_{22}H_{52}O_4P_4Mo$	$C_{22}H_{52}O_4P_4W_2{\cdot}C_4H_{10}O$		$C_{15}H_{44}O_2P_4W$
fw	696.4	1892.8		564.3
system	monoclinic	monoclinic		monoclinic
space group	$P2_1/n$	$P2_1/c$		$P2_1/c$
a, Å	12.117 (8)	14.254 (7)	14.23 (1)	12.813 (2)
b, Å	15.072 (5)	11.922 (3)	11.80 (1)	8.903 (3)
c, Å	17.700 (5)	21.010 (7)	20.58 (2)	21.671 (3)
β, deg	102.18 (3)	105.31 (4)	104.94 (6)	88.62 (1)
V, $Å^3$	3159 (3)	3444 (2)	3339 (3)	2471 (2)
Z	4	4	4	4
ρ(calcd), gcm^{-3}	1.46	1.70	1.88	1.52
μ, cm^{-1}	9.98	70.3	2.95	52.04
		(b) Data Collection		
λ, Å	0.71073	0.71073	0.835	0.71073
scan technique	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
θ scan range, deg	1–25	1–30	0–26	0–29
temp, K	295	295	20	295
rflns collected	5912	5756	5476	3496
independent data	5526	5283	4376	2775
independent data obsd	3500 ($3\sigma(I)$)	4136 ($3\sigma(I)$)	2702 ($2\sigma(I)$)	1963 ($3\sigma(I)$)
		(c) Refinement		
R, %	3.2	4.4	3.4	4.8
R_w,%	3.6	5.3	5.9	5.7
av shift/error	0.087	0.036	0.05	0.15
data/param	11.8	18.0	3.2	14.1

(70% yield), and a mixture of *cis*-$Mo(CO)_2(PMe_3)_4$ and *fac*- and *mer*-$Mo(CO)_3(PMe_3)_3$.[32]

Single-Crystal X-ray Diffraction Studies of 3, 4, and 6. Crystal data and the parameters used during the collection and refinement of the diffraction data for 3, 4, and 6 are summarized in Table III. The X-ray crystal structures of 3 and 4 were determined at the University of Madrid; the structure of 6 was determined at the University of Sevilla. Single crystals of 3, 4, and 6 were introduced into Lyndeman capillaries, sealed under a N_2 atmosphere, and mounted on a Nonius CAD-4 diffractometer.

The cell dimensions for 3 and 4 were refined by least-squares fitting of the θ values of 25 reflections. There was appreciable change in the periodically monitored standard reflections due to radiation damage in both cases. The intensities were scaled up from this decay at the end of the data collection and corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Mo, W, and P were taken from ref 35. Both structures were solved by Patterson and Fourier syntheses, and an empirical absorption correction[36] was applied at the end of the isotropic refinement. The final refinements were made with anisotropic thermal motion for the non-hydrogen atoms (except the C atoms of the methyl groups for 4) and fixed isotropic temperature factors and coordinates for H atoms. The final *R* values were 0.048 for 3 and 0.044 for 4. Most of the calculations were carried out with XRAY80.[37]

The unit cell dimensions and intensity corrections of 6 were obtained as for 3 and 4. The structure was solved by conventional Patterson and Fourier techniques. An empirical absorption correction[36] applied at the end of the isotropic refinement led to a conventional *R* value of 0.064. After mixed full-matrix least-squares refinement with isotropic thermal parameters for P5, O8, C9, C10, C21, C23, C31, C33, C42, C51, C52, and C53, minimizing $\sum w(|F_o| - |F_c|)^2$, an *R* value of 0.052 was obtained. Scattering factors were taken from ref 35. The metal bonded hydrogen atoms could not be located in a difference Fourier map. A final refinement cycle led to *R* = 0.048. The calculations were performed with CRYSTALS.[38]

Single-Crystal Neutron Diffraction Study of 4. Crystal data and the parameters used during the collection and refinement of the diffraction data for 4 are summarized in Table III. Measurements were carried out on the D9B four-circle diffractometer situated at the hot source beam of the Institute Laue Langevin reactor. A low-temperature experiment (20 K) has been chosen in order to minimize the perturbation due to the large thermal motion of the methyl groups of the phosphine ligands. A transparent crystal was sticked at the end of an aluminum pin which was then screwed at the cold end of the displex cryostat mounted on the Eulerian cradle.[39] The cell parameters and the orientation of the crystal were determined by least-squares refinement based on the setting angles of 13 reflections ($13° < \theta < 26°$). In order to avoid a change in the crystallographic symmetry during cooling, reflections up to $\theta = 15°$ was measured by assuming triclinic symmetry. The data were reduced to structure factors according to the Lehmann–Larsen method,[40] and a correction of intensity was then done according to the variation in intensity of standards during measurement. Absorption corrections were made by using numerical integration over the volume of the crystal.[41] The absorption coefficient was calculated by taking into account the incoherent scattering of the hydrogen atoms. The symmetry-related reflections were averaged, and neutron scattering lengths were taken from Bacon.[15] The refinements were performed on F^2 with the weighting scheme $w = 1/[\sigma^2(I) + (0.04I)^2]^{1/2}$. The starting parameters of non-hydrogen atoms were taken from the X-ray structure, and the hydrogen atoms were obtained from Fourier synthesis. A disorder of the solvent molecule Et_2O appeared during the refinements around the inversion center. Difficulties occur in solving this disorder because of the superposition of carbon and hydrogen atoms, their scattering length being of opposite sign. If the solution proposed is the most likely, there still exits significant residues in the synthesis Fourier map. Nevertheless the main molecule is pretty well determined. Anisotropic thermal parameters were introduced for all atoms except those of the ether solvent and the tungsten atoms. A test of secondary extinction has shown that if extinction is present, it shows a second-order effect as compared to the perturbation due to the disorder of ether. Consequently, no extinction has been taken into account.

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Registry No. 1, 82044-79-9; 2, 84879-23-2; 3, 97732-43-9; 4, 122214-24-8; 4*, 122214-26-0; 5, 97749-40-1; 6, 118084-23-4; 7, 122214-25-9; 8, 104413-70-9; 8*, 122214-27-1; 9, 118199-35-2; 10, 118084-28-9; CO_2, 124-38-9; $^{13}CO_2$, 1111-72-4; *trans,mer*-W-$(C_2H_4)_2(CO)(PMe_3)_3$, 98720-85-5; $LiOOCCH{=}CH_2$, 13270-28-5; $LiOOCCH_2CH_3$, 6531-45-9; $WH_2Cl_2(PMe_3)_4$, 87738-93-0; $MoCl_4(PMe_3)_3$, 95797-64-1; $WCl_4(PMe_3)_3$, 73133-10-5; Mo-$(CO_3)(CO)(PMe_3)_4$, 85405-73-8; $W(CO_3)(CO)(PMe_3)_4$, 122214-28-2; *trans*-$Mo(CO)_2(PMe_3)_4$, 122292-34-6; $[Mo(CO_3)(CO)(PMe_3)_3]_2$, 85405-74-9; $MoH_4(PMe_3)_4$, 82456-14-2; *cis*-$Mo(CO)_2(PMe_3)_4$, 30513-06-5; *fac*-$Mo(CO)_3(PMe_3)_3$, 19195-94-9; *mer*-$Mo(CO)_3$-$(PMe_3)_3$, 30513-05-4.

Supplementary Material Available: Tables of more bond distances and angles for 3, 4 (X-ray), and 4 (neutron) and tables of atomic fractional coordinates and anisotropic thermal parameters for 3, 4 (X-ray and neutron), and 6 (18 pages); listings of structure factors for 3, 4 (X-ray), 4 (neutron), and 6 (104 pages). Ordering information is given on any current masthead page.

Origin of the Distinctly Different Gas-Phase Chemistry of Linear and α-Branched Aliphatic Nitriles with Bare Iron(I) Ions. Evidence for Oxidative Addition of the C–CN Bond to Fe^+, New Mechanisms for the Reductive Eliminations of Alkanes, and a Demonstration of Consecutive CH/CC Bond Activations of Different Sites of Flexible Molecules[†]

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For the first time unequivocal evidence is presented demonstrating that α-branched nitriles, in addition to the well-established remote functionalization of C–H bonds, are susceptible to oxidative addition of the C–CN bond to bare Fe^+. The so-formed intermediates give rise to several remarkable processes, the most prominent among which corresponds to the generation of methane. The study of many model systems including a large set of labeled compounds provides detailed insight which permits (i) the suggestion of a new mechanism of Fe^+-mediated methane formation and (ii) the definition of the structural requirements and limitations that dictate whether in RCN/Fe^+ complexes the Fe^+ is inserted in the R–CN bond or remote functionalization of C–H bonds occurs. Evidence is also presented showing that Fe^+-induced loss of "C_nH_{2n+2}" (n = 2, 3) from $(n\text{-}C_6H_{13})_2CHCN$ consists of the consecutive eliminations of C_nH_{2n} and H_2 involving both alkyl chains. While the olefin is generated from the ω- and (ω − 1)-positions of one alkyl chain, the hydrogen molecule originates from the ω′- and (ω′ − 1)-positions of the *other* alkyl chain ("double remote functionalization").

Introduction

Gas-phase experiments with "bare" transition-metal ions offer an unique possibility to probe, in the absence of any solvation and ion-pairing effects, the intrinsic properties of reactive organometallic species and to evaluate the potential role these remarkable transients may play in the initial steps of the activation of C–H and C–C bonds. This topic is, not surprisingly, of fundamental interest in catalysis and has attracted considerable attention in the last decade.[1,2]

Many reactions of transition-metal ions, M^+, with organic substrates can be described by a mechanism (Scheme I) suggested or the first time by Allison and Ridge.[3] Oxidative addition of the C–X bond of the organic substrate 1 to M^+ generates 2 from which, via β-hydrogen transfer, the olefin hydrido complex 3 is generated; depending on the binding energies, 3 then undergoes either

Table I. Metastable Ion (MI) Mass Spectra of RCN/Fe^+ Complexes[a]

R–CN	loss of H_2	C_2H_4	$RCH{=}CH_2$	CH_4	RH	Fe^+
C_2H_5						100
C_3H_7	4	41				55
C_4H_9	75	21				4
C_5H_{11}	92	8				
C_6H_{13}	72	21	2[b]	5		
C_7H_{15}	59	32	6[b]	3		
C_9H_{19}	29	30	35[c]	5	1[d]	
$C_{10}H_{21}$	29	16	46[e]	6	3[f]	

[a] Intensities are expressed in the $\sum$fragment ions = 100%. The alkyl group is always unbranched. [b] R = CH_3. [c] R = CH_3 and R = C_2H_5 contribute in a ratio of 5.8:1 to the overall formation of $RCH{=}CH_2$. [d] R = C_2H_5. [e] R = CH_3, C_2H_5, and C_3H_7 contribute in ratios of 20:12:1 to the overall formation of $RCH{=}CH_2$. [f] C_2H_6, C_3H_8, and C_4H_{10} are formed in a roughly 1:1:1 ratio.

[†] Dedicated to Professor Rolf Huisgen, Universität München, in honor of his pioneering work and fundamental contributions to physical organic chemistry.

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