of the 3·pyrene complex (for the concentrations of host and guest see Table II).

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Registry No. **2**, 92816-67-6; **2**·perylene, 100928-41-4; **2**·pyrene, 92816-68-7; **2**·naphthalene, 100928-42-5; **3**, 92787-69-4; **3**·perylene, 100928-38-9; **3**·pyrene, 100928-39-0; **3**·fluoranthene, 100938-76-9; **3**·naphthalene, 100928-40-3; **3**·durene, 100938-77-0; **4**, 92787-65-0; **5**, 92787-66-1; **6**, 92787-58-1; **7**, 92787-59-2; **8**, 92787-60-5; **9**, 92787-61-6; **10**, 92787-62-7; **11**, 92787-63-8; **12**, 92787-64-9; **13**, 92816-66-5; **14**, 92787-67-2; **15**, 92787-68-3; **16**·perylene, 100928-43-6; **16**·pyrene, 100928-44-7; **16**·fluoranthene, 100928-45-8; **16**·naphthalene, 100928-46-9; 1-acetyl-4,4-bis(4-hydroxy-3,5-dimethylphenyl)piperidine, 86748-12-1; ethyl α-bromoacetate, 105-36-2; *N*-hydroxysuccinimide, 6066-82-6; benzyl chloroformate, 501-53-1.

Carbon Dioxide Chemistry. Synthesis, Properties, and Structural Characterization of Stable Bis(carbon dioxide) Adducts of Molybdenum

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Abstract: The bis(carbon dioxide) adduct, *trans*-$Mo(CO_2)_2(PMe_3)_4$, **1**, has been prepared from the reaction of *cis*-$Mo(N_2)_2(PMe_3)_4$ with CO_2 under pressure (4–5 atm). The interaction of **1** with several small molecules has been studied. In particular, reaction with COS affords a seven-coordinate *S,S'*-dithiocarbonate, $Mo(S_2CO)(CO)_2(PMe_3)_3$, **2**, while interaction with various isocyanides yields the new carbon dioxide complexes *trans,mer*-$Mo(CO_2)_2(CNR)(PMe_3)_3$, **3** (R = Me, **3a**; *i*-Pr, **3b**; *t*-Bu, **3c**; Cy, **3d**; $CH_2C_6H_5$, **3e**). The new compounds have been characterized by analytical and spectroscopic (IR and ^1H, ^{13}C, and ^{31}P NMR) studies. The molecular structures of **2**, **3b**, and **3e** have been determined by X-ray crystallography. Compound **2** is orthorhombic and belongs to the space group $Pna2_1$ with $a = 14.003$ (2) Å, $b = 9.767$ (2) Å, $c = 15.127$ (2) Å, $D_c = 1.52$ g·cm^{-3}, and $Z = 4$. Refinement was achieved on 1939 independent observed reflections, leading to a final R value of 0.038. **3b** crystallizes in the monoclinic space group $C2/c$ with unit cell parameters $a = 24.47$ (3) Å, $b = 13.01$ (1) Å, $c = 16.77$ (1) Å, $\beta = 132.41$ (3)°, and $D_c = 1.35$ g·cm^{-3} for $Z = 8$. Least-squares refinement based on 3493 independent observed reflections led to a final R value of 0.076. Crystals of **3e** are monoclinic, space group $P2_1/c$ with $a = 11.563$ (8) Å, $b = 11.792$ (7) Å, $c = 18.57$ (1) Å, $\beta = 90.42$ (4)°, $D_c = 1.39$ g·cm^{-3}, and $Z = 4$, 1907 reflections were considered observed ($I \geq 3\sigma(I)$), and the final R value based on them was 0.093. **3b** and **3e** are isostructural, with the Mo atom bonded to two trans, staggered CO_2 molecules, the overall molecular geometry being approximately octahedral.

Molecular carbon dioxide complexes of transition metals have received considerable attention in the past years, in the hope of discovering model systems for the activation of CO_2 and its subsequent transformation into organic chemicals of commercial interest. Despite considerable and intensive research, attested by the number of review articles published in this subject in recent years,[2] only a few compounds have been authenticated as true carbon dioxide complexes. These include species containing side-on η^2-coordinated[3] and η^1,C-coordinated[4] CO_2, as well as two examples of what is usually referred to as assisted coordination of carbon dioxide.[5] In addition, numerous reports have appeared[6] on CO_2 complexes whose structures have been proposed on the basis of spectroscopic and chemical evidences. A closer examination of these complexes[7] discredited many of the initial formulations, and this, the difficulty in the spectroscopic characterization (due in part to the paucity of information on IR and NMR data for authentic CO_2 complexes), and other factors led Ibers to propose[2d,8] structural determination by diffraction methods as the only criterion to adequately characterize transition metal–carbon dioxide complexes.

The continuous interest in carbon dioxide chemistry, and the existence of only a brief report on the reaction of this molecule with dinitrogen complexes of molybdenum,[9] prompted us to investigate its interaction with the complex *cis*-$Mo(N_2)_2(PMe_3)_4$,

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which had been recently prepared in our laboratory.[10] In the present contribution, we wish to present a complete account of the work carried out on this system, which has led to the preparation of *trans*-$Mo(CO_2)_2(PMe_3)_4$, **1**, and its characterization as the first stable bis(carbon dioxide) adduct of a transition metal. The reactions of **1** with COS, to afford $Mo(S_2CO)(CO)_2(PMe_3)_3$, **2**, which has been studied by X-ray crystallography, and with various isocyanides, to produce new CO_2 complexes, *trans,mer*-$Mo(CO_2)_2(CNR)(PMe_3)_3$ (R = Me, **3a**; *i*-Pr, **3b**; *t*-Bu, **3c**; Cy, **3d**; $CH_2C_6H_5$, **3e**), are also reported. Complexes **1** and **3a**–**3e** contain two CO_2 ligands bonded to the molybdenum atom in a dihapto manner through one of the C=O bonds, as conclusively demonstrated by X-ray structural determinations carried out on complexes **3b** and **3e**. Finally, a reinvestigation of the reaction of *cis*-$Mo(N_2)_2(PMe_2Ph)_4$[9] with CO_2 has been effected and the results reported. Part of this work has appeared in preliminary form,[11] and while our work was in progress, a brief report concerning a possible CO_2 complex of molybdenum has been published.[12]

Results and Discussion

Synthesis of *trans*-$Mo(CO_2)_2(PMe_3)_4$ (1). Diluted petroleum ether solutions (ca. 10^{-2} M) of *cis*-$Mo(N_2)_2(PMe_3)_4$ absorb 2 mol of carbon dioxide per mole of the molybdenum complex, at room temperature and pressure, with the formation of complex **1** (eq 1). The absorption of CO_2 is irreversible and yields yellow

$$cis\text{-}Mo(N_2)_2(PMe_3)_4 + 2CO_2 \rightarrow trans\text{-}Mo(CO_2)_2(PMe_3)_4 + 2N_2 \quad (1)$$

microcrystals of **1** in good yields. Smaller amounts of the disproportionation products $Mo(CO_3)(CO)(PMe_3)_4$ and $[Mo(CO_3)(CO)(PMe_3)_3]_2$[13] are also produced, but their formation can be minimized by carrying out the reaction under 4–5 atm of carbon dioxide. Under these conditions, complex **1** can be isolated in ca. 80% yield. Formation of the disproportionation products is, however, preferred if the reaction is carried out in coordinating solvents or in the presence of free PMe_3.[11a]

In contrast with the behavior shown by other CO_2 complexes,[3a,5a] **1** is stable toward loss of CO_2 at room temperature, both in solution and in the solid state. As a solid, it can be heated under vacuum at 50 °C for several hours without noticeable decomposition, but in solution it decomposes slowly at 20 °C, even under inert atmosphere, although decomposition is prevented by the addition of PMe_3. Analytical and molecular weight determinations for **1** are in accord with the proposed formulation but provide no information with regard to the bonding mode of the CO_2 molecules. Since efforts to grow crystals suitable for X-ray studies have proved unsuccessful, in order to ascertain the structural characteristics of **1**, a detailed investigation of its spectroscopic and chemical properties has been undertaken.

Spectroscopic Properties of 1. Due to the limited number of structurally characterized transition metal–carbon dioxide complexes, and hence to the paucity of reliable IR and NMR data for these compounds, spectroscopic evidence for M–CO_2 coordination should be considered very carefully. Indeed, as already indicated, a number of CO_2 derivatives formulated as such on the basis of chemical and spectroscopic evidences were later shown to be otherwise.[7]

Complex **1** displays IR bands at 1670, 1155, and 1100 cm^{-1} (Figure 1). A comparison with the spectrum of **1*** (50% $^{13}CO_2$-enriched) clearly demonstrates that these bands are due to vibrations arising from the coordinated CO_2 molecules, but no conclusions as to the coordination mode of the CO_2 ligands can be inferred. Thus, although similar data have been reported for the η^2-CO_2 complexes $Ni(PCy_3)_2(CO_2)$,[3a] $Nb(C_5H_4Me)_2(CH_2SiMe_3)(CO_2)$,[3b] and $[Cp_2Mo(CO_2)]_n$[3c] in other CO_2 compounds containing C-bonded η^1-carbon dioxide, the CO_2 ligands give rise to absorptions of similar energies (for instance, 1610 and 1210 cm^{-1} in $Rh(diars)_2Cl(\eta^1\text{-}CO_2)$[4] and 1680, 1278, and 1212 cm^{-1} in $Co(salen)Na(CO_2)$[5a]). Furthermore, some carbonato[13,14] and other complexes resulting from various transformations[15] of coordinated CO_2 give rise to IR bands in the regions 1700–1600 and 1250–1100 cm^{-1}. It becomes, therefore, evident that IR data, per se, have very little value to attest CO_2 coordination in its intact form to a transition metal.

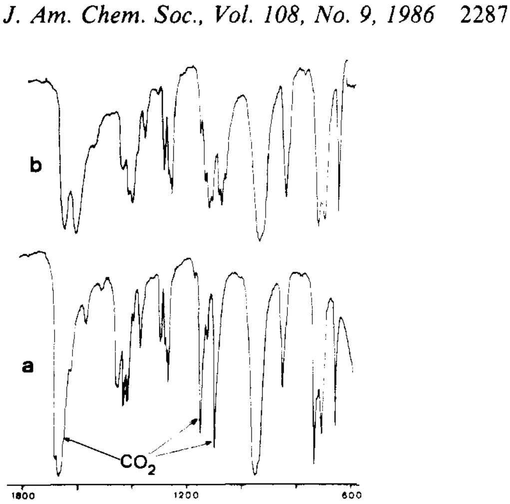
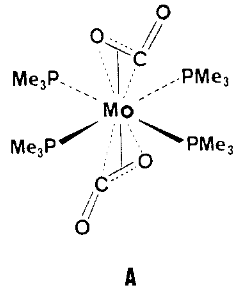


Figure 1. Infrared spectra of *trans*-$Mo(CO_2)_2(PMe_3)_4$: (a) natural isotopic abundance; (b) ca. 50% $^{13}CO_2$-enriched. The arrows indicate the absorptions due to the CO_2-metal-bonded groups.

^{31}P and ^{13}C NMR studies are more informative. At 30 °C, the 24.3-MHz $^{31}P\{^1H\}$ NMR spectrum of **1** is a slightly broad signal, which becomes a sharp singlet at 50 °C. Upon cooling, the singlet converts into a pattern of lines which at −40 °C correspond to an AA′BB′ spin system. This is best observed in the 101.4-MHz spectrum at −60 °C, from which characteristic NMR parameters (see Experimental Section) have been computed. On the other hand, the ^{13}C NMR spectrum of **1*** displays a quintet, at 206.1 ppm ($^2J_{CP}$ = 18 Hz) due to the CO_2 ligands. In addition, the 24.3-MHz $^{31}P\{^1H\}$ NMR spectrum of **1*** recorded at 60 °C, although partially unresolved due to decomposition of the sample, clearly shows the three central lines of the 1:4:6:4:1 quintet expected for an isotopic mixture containing approximately 25% molecules of $Mo(^{13}CO_2)_2(PMe_3)_4$, 25% $Mo(CO_2)_2(PMe_3)_4$, and 50% $Mo(^{13}CO_2)(CO_2)(PMe_3)_4$. The separation of the outer lines of the observed triplet gives a value of 17.5 Hz for $^2J_{CP}$, in excellent agreement with that deduced from the ^{13}C spectrum. From the above data, a ground-state structure A can be proposed, in which the coordinated C=O bonds are staggered with respect to one another and eclipsed with regard to the *trans*-P–Mo–P vectors of the equatorial plane, in a manner similar to that found for the ethylene molecules in the complexes *trans*-$Mo(C_2H_4)_2L_4$ (L_2 = dppe,[16] L = PMe_3[10]). A fluxional process, probably involving



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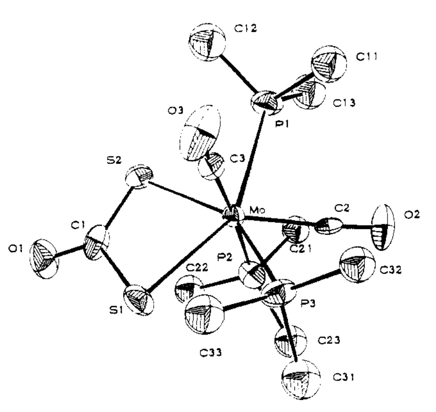

Figure 2. Molecular structure of $Mo(S_2CO)(CO)_2(PMe_3)_3$, **2**, with the atoms represented by their 50% probability ellipsoids for thermal motion.

rotation of the CO_2 ligands, is clearly responsible for the temperature dependence of the NMR spectra. Further confirmation for this structure comes from the facile conversion of **1** into complexes **3a**–**3e**, of which **3b** and **3e** have been characterized by X-ray studies (see below).

It is worth mentioning at this point that all the compounds $Ni(PCy_3)_2(CO_2)$,[3a] $Nb(C_5H_4Me)(CH_2SiMe_3)(CO_2)$,[3b] $[Cp_2Mo(CO_2)]_n$,[3c] **1**, and **3a**–**3e**, which contain side-on coordinated CO_2, show a strong IR band at 1750–1650 cm^{-1} and a ^{13}C resonance at 210–195 ppm, due to the CO_2 ligands (no ^{13}C data have been reported for $Ni(PCy_3)_2(CO_2)$[3a] and $[Cp_2Mo(CO_2)]_n$[3c]). It seems, therefore, reasonable that a combination of IR and ^{13}C NMR data can be used as a diagnosis for dihapto coordination of CO_2 to a transition metal. Further studies on already known and new transition metal–carbon dioxide complexes are desirable to confirm this hypothesis and to spectroscopically ascertain other bonding modes of this molecule.

Chemical Properties of *trans*-$Mo(CO_2)_2(PMe_3)_4$ (1). X-ray Structure of $Mo(S_2CO)(CO)_2(PMe_3)_3$ (2). The reaction of **1** with MeI or I_2 produces $MoI_2(PMe_3)_4$,[17] with liberation of CO_2. In contrast with the behavior found for other CO_2 complexes[3a,5a,18] substitution of the CO_2 ligands by N_2, C_2H_4, and other small molecules does not take place at appreciable rate under ambient conditions, while interaction with CO (20 °C, 30 min) produces *cis*-$Mo(CO)_2(PMe_3)_4$ and CO_2. When complex **1** is reacted with COS, a yellow crystalline solid displaying IR bands at 1690 and 1570 cm^{-1}, which may be due[19] to a S_2CO^{2-} ligand, is obtained. Since NMR and other data are inconclusive with regard to the molecular complexity of **2**, an X-ray determination has been carried out. This has shown that the complex has formula $Mo(S_2CO)(CO)_2(PMe_3)_3$ and contains a S_2CO^{2-} group resulting from the reductive disproportionation[20] of two COS molecules induced by the metal complex. Compound **2** is best obtained by reaction of COS with *cis*-$Mo(N_2)_2(PMe)_4$.

Figure 2 shows an ORTEP view of **2**. The molecular structure is best described in terms of a pentagonal bipiramid (PB), with the axial positions occupied by one carbonyl and one PMe_3 ligands. The major distorsions from the ideal PB geometry are found in the equatorial sites and consist of some bending of the Mo–P(1) and Mo–P(3) bonds toward C(2) and C(3) simultaneously and some bending of the Mo–S(1), Mo–S(2), and Mo–C(2) bonds toward P(2). This obviously causes a decrease in the overcrowding of the ML_5 girdle, lessening the steric interactions. These steric interactions tend to yield, for the same ligand, a greater M–L bond distance for the equatorial sites, as compared with the less-crowded axial sites,[21] and yet, as can be appreciated in Table I, the axial CO and PMe_3 groups are characterized by the longest Mo–CO and Mo–PMe_3 bond distances. This may be due to the high, mutual trans influence of these ligands. The C–S bond distances within the planar dithiocarbonate ligand are significantly different (C(1)–S(1), 1.83 (3) Å; C(1)–S(2), 1.68 (3) Å), the latter indicating partial double bond character.[22] Other bond distances and angles within the S_2CO^{2-} group have similar values to those reported for other *S,S'*-dithiocarbonate complexes.[22,23,24]

Table I. Bond Distances (Å) and Angles (deg) for $Mo(S_2CO)(CO)_2(PMe_3)_3$

Mo–P(1)	2.478 (6)	P(2)–C(22)	1.85 (1)
Mo–P(2)	2.620 (2)	P(2)–C(23)	1.72 (2)
Mo–P(3)	2.491 (6)	P(3)–C(31)	1.76 (2)
Mo–S(1)	2.577 (7)	P(3)–C(32)	1.80 (2)
Mo–S(2)	2.533 (7)	P(3)–C(33)	1.92 (2)
Mo–C(2)	1.957 (8)	S(1)–C(1)	1.83 (3)
Mo–C(3)	1.978 (8)	S(2)–C(1)	1.68 (3)
P(1)–C(11)	1.86 (2)	C(1)–O(1)	1.236 (12)
P(1)–C(12)	1.75 (2)	C(2)–O(2)	1.15 (1)
P(1)–C(13)	1.91 (2)	C(3)–O(3)	1.16 (1)
P(2)–C(21)	1.94 (2)		
P(1)–Mo–P(2)	107.2 (2)	Mo–P(1)–C(13)	118.0 (5)
P(1)–Mo–P(3)	124.6 (2)	Mo–P(2)–C(21)	113.8 (5)
P(2)–Mo–P(3)	107.0 (2)	Mo–P(2)–C(22)	120.0 (3)
P(1)–Mo–S(1)	147.9	Mo–P(2)–C(23)	119.3 (7)
P(1)–Mo–S(2)	81.0 (2)	Mo–P(3)–C(31)	120.4 (6)
P(1)–Mo–C(2)	78.8 (4)	Mo–P(3)–C(32)	119.0 (5)
P(1)–Mo–C(3)	75 (1)	Mo–P(3)–C(33)	111.1 (5)
P(2)–Mo–S(1)	80.0 (2)	C(11)–P(1)–C(12)	103.0 (8)
P(2)–Mo–S(2)	81.5 (2)	C(11)–P(1)–C(13)	101.3 (7)
P(2)–Mo–C(2)	75.2 (2)	C(21)–P(2)–C(22)	97.7 (7)
P(2)–Mo–C(3)	176.5 (3)	C(12)–P(1)–C(13)	100.4 (7)
P(3)–Mo–S(1)	80.2 (2)	C(21)–P(2)–C(23)	100.7 (8)
P(3)–Mo–S(2)	146.4 (2)	C(22)–P(2)–C(23)	101.7 (7)
P(3)–Mo–C(2)	69.4 (4)	C(31)–P(3)–C(32)	102.6 (7)
P(3)–Mo–C(3)	73.5 (10)	C(31)–P(3)–C(33)	98.8 (7)
S(1)–Mo–S(2)	69.0 (2)	C(32)–P(3)–C(33)	101.6 (7)
S(1)–Mo–C(2)	132.5 (4)	Mo–S(1)–C(1)	87.6 (7)
S(1)–Mo–C(3)	96.7 (6)	Mo–C(2)–C(1)	92.3 (8)
S(2)–Mo–C(2)	142.9 (3)	S(1)–C(1)–S(2)	111.0 (5)
S(2)–Mo–C(3)	96.2 (6)	S(1)–C(1)–O(1)	115 (3)
C(2)–Mo–C(3)	108.1 (3)	S(2)–C(1)–O(1)	133 (3)
Mo–P(1)–C(11)	113.1 (6)	Mo–C(2)–O(2)	171 (2)
Mo–P(1)–C(12)	118.5 (6)	Mo–C(3)–O(3)	176.6 (7)

Table II. Selected IR and ^{13}C NMR Data for the New Carbon Dioxide Complexes

		^{13}C NMR	
compound	IR, cm^{-1} [a]	δ[b]	$^2J_{PC}$, Hz[c]
$Mo(CO_2)_2(PMe_3)_4$	1670, 1155, 1100	206.1 q	18
$Mo(CO_2)_2(PMe_3)_3(CNMe)$	1660, 1150, 1100	201.1 m	
$Mo(CO_2)_2(PMe_3)_3(CN\text{-}i\text{-}Pr)$	1675, 1160, 1100	201.4 m	
$Mo(CO_2)_2(PMe_3)_3(CN\text{-}t\text{-}Bu)$	1680, 1155, 1100	201.2 td	18, 11
$Mo(CO_2)_2(PMe_3)_3(CNCy)$	1665, 1150, 1100	201.4 td	18, 11
$Mo(CO_2)_2(PMe_3)_3(CNCH_2Ph)$	1670, 1150, 1100	201.8 m	

[a] Nujol mull. [b] C_6D_6 at 20 °C; m = unresolved multiplet, q = quintet, td = triplet of doublets. [c] Full multiplicity of the $^{13}CO_2$ signals only observed for enriched samples.

Reaction of 1 with Isocyanides. X-ray Structures of *trans*,*mer*-$Mo(CO_2)_2(CNR)(PMe_3)_3$ (R = *i*-Pr and $CH_2C_6H_5$). Complex **1** shows some structural and chemical similarities with the ethylene analogue *trans*-$Mo(C_2H_4)_2(PMe_3)_4$. Recent work carried out in our laboratory[10,25,26] has shown that the ethylene compound

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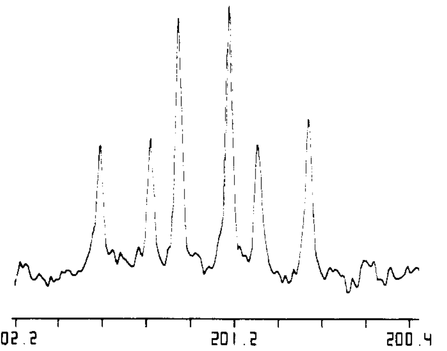

Figure 3. Partial $^{13}C\{^1H\}$ NMR spectrum of *trans,mer*-$Mo(CO_2)_2(CNCy)(PMe_3)_3$, ca. 33% enriched in $^{13}CO_2$, showing the coupling of $^{13}CO_2$ to the three meridional ^{31}P nuclei.

undergoes substitution of one or two PMe_3 groups by CO or CNR to yield new compounds of composition *trans,mer*-$Mo(C_2H_4)_2L(PMe_3)_3$ and *trans,trans,trans*-$Mo(C_2H_4)_2L_2(PMe_3)_2$. Surprisingly, substitution of the C_2H_4 ligands is not observed even under 2–3 atm of CO. In light of these results, a similar behavior was anticipated for complex **1**, and although CO causes displacement of the CO_2 ligands, interaction with various isocyanides affords the new carbon dioxide complexes *trans,mer*-$Mo(CO_2)_2(CNR)(PMe_3)_3$, **3** (R = Me, **3a**; *i*-Pr, **3b**; *t*-Bu, **3c**; Cy, **3d**; $CH_2C_6H_5$, **3e**), as indicated in eq 2. In no case has substitution

$$Mo(CO_2)_2(PMe_3)_4 + CNR \rightarrow Mo(CO_2)_2(CNR)(PMe_3)_3 + PMe_3 \quad (2)$$

of a second PMe_3 or of CO_2 ligands been observed after stirring at room temperature for 2–3 days in the presence of 2 equiv of CNR. With the exceptions of some absorptions arising from the coordinated CNR group, the IR spectra of complexes **3a**–**3e** and **1** are strikingly similar. In particular, the bands at ca. 1670, 1155, and 1100 cm^{-1}, associated with the CO_2 ligands in **1**, have nearly the same frequencies in compounds **3** (Table II), and this indicates that the phosphine substitution reaction takes place without change in the coordination mode of the CO_2 ligands.

NMR spectroscopic studies are in accord with the ground-state trans,mer geometry proposed for compounds **3**, since the PMe_3 ligands give rise to a virtually coupled triplet and a doublet in the ^1H NMR spectrum and to a triplet and a doublet (in some cases partially superimposed) in the $^{13}C\{^1H\}$ NMR spectrum. The $^{31}P\{^1H\}$ NMR spectra of the complexes **3** are also in agreement with the proposed formulation, since they consist of a doublet and a broad, unresolved triplet (intensity ratio 2:1) which become a clear AX_2 pattern at higher temperatures (δ_A −8.4, δ_X 0.4, $^2J_{AX}$ = 19 Hz, data for **3c** at 50 °C). As the parent complex **1**, compounds **3** are fluxional, the process responsible for the observed fluxionality being possibly rotation around the Mo–CO_2 bonds. A detailed investigation of this process by means of variable-temperature ^{13}C and ^{31}P studies is under way. The relatively low solubility of **3a**–**3e**, the long relaxation time of the M–$^{13}CO_2$ ^{13}C nucleus, and the splitting of the ^{13}C resonance of the CO_2 ligands due to coupling to the phosphorus nuclei make difficult the clear observation of the full multiplicity of the CO_2 signals (see Table II for δ_{CO_2} values and other data). Samples of **3c*** and **3e*** were for this reason prepared from **1*** and the corresponding isocyanide, and a clear triplet of doublets, centered at ca. 201 ppm ($^2J_{CP_X}$ = 18, $^2J_{CP_A}$ = 11 Hz) was observed for these complexes, as shown in Figure 3 for **3e**. A determination of the spin–lattice relaxation time of the ^{13}C nuclei in **3e** by the inversion–recovery technique led to a T_1 value of 40 s.

Complexes **3** are yellow, crystalline solids, moderately soluble in diethyl ether and aromatic hydrocarbons, and more soluble in tetrahydrofuran. In comparison with other known CO_2 complexes, they exhibit surprising thermal stability, and for instance, **3b** can be heated at 80 °C for several hours, under vacuum or under nitrogen, without noticeable decomposition. In contrast to the behavior found for **1** (see above), toluene solutions of compounds **3** do not decompose at room temperature for periods of 3–4 days when kept under N_2, although extensive decomposition occurs at 60 °C. The enhanced stability of derivatives **3** toward ligand dissociation, as compared with **1**, is likely due to a decrease both in the electron density at the metal and in the steric repulsions of the ligands, which is to be expected upon substitution of the basic, more steric demanding[27] PMe_3 ligand (θ = 118°) by the strong π-acceptor, less steric demanding ($\theta \simeq 100°$) CNR group.

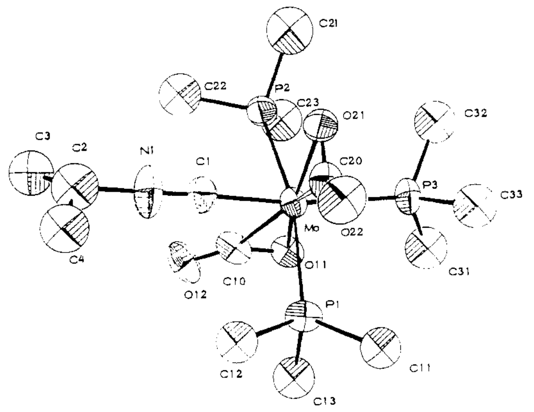

Figure 4. ORTEP diagram and atom labeling scheme for *trans,mer*-$Mo(CO_2)_2(CN\text{-}i\text{-}Pr)(PMe_3)_3$.

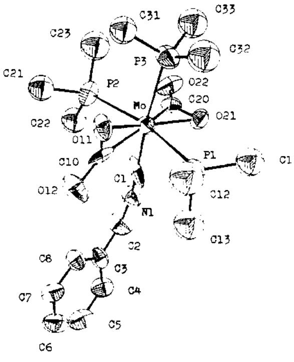

Figure 5. Molecular structure and atom labeling scheme for *trans,-mer*-$Mo(CO_2)_2(CNCH_2Ph)(PMe_3)_3$.

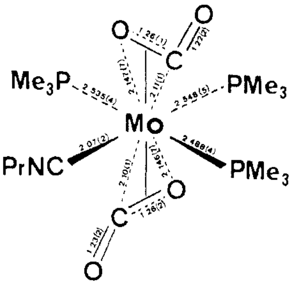

Figure 6. Interatomic distances in *trans,mer*-$Mo(CO_2)_2(CN\text{-}i\text{-}Pr)(PMe_3)_3$.

The crystal structures of **3b** and **3e** have been determined by X-ray crystallography, ORTEP views for these complexes are shown in Figures 4 and 5, and interatomic distances and bond angles are shown in Tables III and IV. The compounds are isostructural and have distorted octahedral geometries, with the CO_2 ligands dihapto bonded to the metal atoms through one of the C=O bonds. Interestingly, the coordinated double bonds exhibit the staggered–eclipsed conformation (the first term applies to the relative orientation of the coordinated C=O bonds, while the second defines the position of these axial bonds with respect to the *trans*-P–Mo–L (L = P and C) vectors of the equatorial plane)

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Table III. Bond Distances (Å) and Angles (Å) for $Mo(CO_2)_2(CN\text{-}i\text{-}Pr)(PMe_3)_3$

Mo–O(11)	2.146 (7)	N(1)–C(2)	1.50 (4)
Mo–C(10)	2.10 (1)	C(2)–C(3)	1.43 (4)
Mo–O(21)	2.147 (7)	C(2)–C(4)	1.37 (3)
Mo–C(20)	2.11 (1)	P(1)–C(11)	1.83 (2)
Mo–C(1)	2.07 (2)	P(1)–C(12)	1.83 (2)
Mo–P(1)	2.488 (4)	P(1)–C(13)	1.83 (2)
Mo–P(2)	2.535 (4)	P(2)–C(21)	1.80 (1)
Mo–P(3)	2.548 (5)	P(2)–C(22)	1.81 (3)
O(11)–C(10)	1.26 (2)	P(2)–C(23)	1.79 (2)
C(10)–O(12)	1.22 (2)	P(3)–C(31)	1.83 (3)
O(21)–C(20)	1.26 (1)	P(3)–C(32)	1.81 (2)
C(20)–O(22)	1.22 (1)	P(3)–C(33)	1.72 (3)
C(1)–N(1)	1.14 (3)		
P(2)–Mo–P(3)	93.3 (1)	O(11)–C(10)–O(12)	133 (1)
P(1)–Mo–P(3)	94.1 (2)	Mo–C(10)–O(12)	152 (1)
P(1)–Mo–P(2)	162.7 (1)	Mo–O(21)–C(20)	71.4 (7)
C(1)–Mo–P(3	167.9 (3)	Mo–C(20)–O(21)	74.3 (6)
C(1)–Mo–P(2)	87.2 (4)	O(21)–C(20)–O(22)	134 (1)
C(1)–Mo–P(1e	88.8 (4)	Mo–C(20)–O(22)	152 (1)
C(20)–Mo–P(3)	88.1 (4)	Mo–C(1)–N(1)	178 (1)
C(20)–Mo–P(2)	117.5 (4)	C(1)–N(1)–C(2)	177 (2)
C(20)–Mo–P(1)	78.3 (4)	M(1)–C(2)–C(4)	111 (2)
C(20)–Mo–P(1)	81.0 (5)	M(1)–C(2)–C(3)	110 (2)
O(21)–Mo–P(3)	84.8 (2)	C(3)–C(2)–C(4)	135 (2)
O(21)–Mo–P(2)	83.6 (3)	Mo–P(1)–C(13)	115.5 (5)
O(21)–Mo–P(1)	112.6 (3)	Mo–P(1)–C(12)e	113.4 (7)
O(21)–Mo–C(1)	83.2 (4)	Mo–P(1)–C(11)	121.6 (5)
O(21)–Mo–C(20)	34.2 (4)	C(12)–P(1)–C(13)	102.1 (7)
C(10)–Mo–P(3)	115.3 (3)	C(11)–P(1)–C(13)	101.5 (9)
C(10)–Mo–P(2)	80.7 (4)	C(11)–P(1)–C(12)	99.9 (7)
C(10)–Mo–P(1)	82.0 (4)	Mo–P(2)–C(23)	116.5 (9)
C(10)–Mo–C(1)	76.7 (5)	Mo–P(2)–C(22	115.0 (6)
C(10)–Mo–C(20)	150.4 (4)	Mo–P(2)–C(21)	117.7 (7)
C(10)–Mo–O(21)	155.0 (6)	C(22)–P(2)–C(23)	102.2 (9)
O(11)–Mo–P(3)	80.8 (2)	C(21)–P(2)–C(23)	104.3 (9)
O(11)–Mo–P(2)	83.5 (3)	C(21)–P(2)–C(22)	99 (1)
O(11)–Mo–P(1)	82.3 (2)	Mo–P(3)–C(33)	116.2 (8)
O(11)–Mo–C(1)	111.1 (4)	Mo–P(3)–C(32)	119 (1)
O(11)–Mo–C(20)	156.9 (6)	Mo–P(3)–C(31)	117.1 (7)
O(11)–Mo–O(21)	160.1 (3)	C(32)–P(3)–C(33)	104 (1)
O(11)–Mo–C(10)	34.5 (4)	C(31)–P(3)–C(33)	102 (1)
Mo–O(11)–C(10)	70.7 (6)	C(31)–P(3)–C(32)	95.6 (9)
Mo–C(10)–O(11)	74.8 (6)		

Table IV. Bond Lengths (Å) and Bond Angles (deg) for $Mo(CO_2)_2(PMe_3)_3\ (CN–CH_2–C_6H_5)$

Mo–C10	2.02 (2)	P2–C21	1.82 (2)
Mo–O11	2.14 (1)	P2–C22	1.81 (3)
Mo–C20	2.02 (2)	P2–C23	1.83 (3)
Mo–O21	2.16 (1)	P3–C31	1.79 (2)
Mo–P1	2.515 (6)	P3–C32	1.82 (2)
Mo–P2	2.493 (6)	P3–C33	1.78 (3)
Mo–P3	2.566 (6)	C1–N1	1.21 (2)
Mo–C1	2.03 (1)	N1–C2	1.42 (2)
C10–O11	1.25 (2)	C2–C3	1.51 (3)
C10–O12	1.28 (3)	C3–C4	1.39 (3)
C20–O21	1.20 (2)	C3–C8	1.35 (3)
C20–O22	1.28 (3)	C4–C5	1.39 (3)
P1–C11	1.82 (2)	C5–C6	1.35 (3)
P1–C12	1.81 (3)	C6–C7	1.39 (3)
P1–C13	1.82 (3)	C7–C8	1.35 (3)
C10–Mo–O11	34.8 (6)	P2–Mo–C1	87.1 (6)
C10–Mo–C20	150.5 (6)	P3–Mo–C1	169.4 (6)
O11–Mo–O21	160.5 (5)	O11–C10–O12	128 (2)
C10–Mo–P1	83.3 (6)	O21–C20–O22	128 (2)
C10–Mo–P2	81.3 (6)	Mo–P1–C11	116.9 (9)
C10–Mo–P3	115.1 (5)	Mo–P1–C12	119.7 (9)
C10–Mo–C1	75.4 (7)	Mo–P1–C13	113.1 (9)
C20–Mo–P1	113.8 (6)	C11–P1–C12	104 (1)
C20–Mo–O21	33.2 (6)	C11–P1–C13	100 (1)
C20–Mo–P2	80.0 (6)	C12–P1–C13	100 (1)
C20–Mo–P3	88.5 (5)	Mo–P2–C21	115.7 (8)
C20–Mo–C1	81.0 (8)	Mo–P2–C22	113.4 (9)
P1–Mo–P2	164.6 (2)	Mo–P2–C23	118.4 (8)
P1–Mo–P3	94.4 (2)	C21–P2–C22	103 (1)
P1–Mo–C1	88.4 (6)	C21–P2–C23	103 (1)
P2–Mo–P3	92.8 (2)	C22–P2–C23	102 (1)
Mo–P3–C31	112.1 (8)	N1–C2–C3	115 (2)
Mo–P3–C32	121.6 (10)	C2–C3–C4	115 (1)
Mo–P3–C33	115.6 (9)	C2–C3–C8	123 (2)
C31–P3–C32	98 (1)	C4–C3–C8	122 (2)
C31–P3–C33	107 (1)	C3–C4–C5	117 (2)
C32–P3–C33	100 (1)	C4–C5–C6	120 (2)
Mo–C1–N1	179 (2)	C5–C6–C7	122 (2)
C1–N1–C2	170 (2)	C6–C7–C8	119 (2)

found by Osborn,[16] Veillard,[28] and us[10] for analogous ethylene derivatives. It is therefore evident that in these complexes, C,O-bonded CO_2 and ethylene have the same stereochemical preferences.

A consideration of bond distances within the Mo–η^2-CO_2 units[29] (Figure 6) reveals strong Mo–CO_2 bonding interactions. The Mo–C bond lengths in **3b** average 2.105 (10) Å, a value which is only slightly longer than the Mo–CNR distance in the same complex and considerably shorter than the Mo–C (ethylene) distances found in the analogous complexes[10] *trans*-Mo($C_2H_4)_2(PMe_3)_4$ and *trans*,*mer*-Mo($C_2H_4)_2$(CO)($PMe_3)_3$ (2.270 (5) and 2.29 (3) Å, respectively). These Mo–CO_2 distances approach normal molybdenum–carbonyl distances (1.952 (6) Å in the latter complex; 1.970 (4) and 2.03 (1) Å, average for the two types of CO ligands in *cis*-Mo(CO)$_4$(PMe$_3$)$_2$ [30]). Since the Mo–η^2-CO_2 fragments can be considered structurally similar to Mo–dihaptoacyl units, a comparison of bond parameters for both units is worthy at this point. The main difference between the two structures lies in the Mo–O separations (and related bond angles) which are only 2.147 (7) and 2.15 (1) Å in **3b** and **3e**, while they range between 2.287 (2) and 2.324 (4) Å in dihaptoacyl derivatives.[31-33] The latter values are indicative of single Mo–O bonds.[31] The Mo–C bond lengths in Mo–C(O)R complexes are found in the range 1.996 (9)–2.005 (2) Å, only slightly shorter than the Mo–C bonds in **3b**, and of the same order of magnitude[29] than in **3e**. As indicated above, these short Mo–C and Mo–O contacts in the CO_2 complexes are indicative of strong Mo–CO_2 binding. Related to these distances are the coordinated C=O bond lengths, which are of the same order of magnitude for the two types of complexes (ca. 1.26 (2) Å for **3b**; 1.225 (4)–1.267 (11) Å in the dihaptoacyl complexes). Similarly, the O–C–O and C–Mo–O angles in the CO_2 complexes (133.5° and 34.5°, respectively) compare well with the corresponding R–C–O and C–Mo–O angles in the dihaptoacyl derivatives (127° and 32°).

The Mo–P distances found in **3b** and **3e** can be considered long for trimethylphosphine complexes of molybdenum(0).[34] The two mutually *trans*-PMe$_3$ ligands have average Mo–P separations of 2.51 (2) and 2.50 (1) Å, respectively, while the PMe$_3$ groups trans to the isocyanide ligands are 2.548 (5) and 2.566 (6) Å (**3b** and **3e**) apart from the molybdenum atom. The Mo–CNC entities are almost linear (Mo–C(1)–N(1), 178.5 (9)°; C(1)–N(1)–C(2), 177(1)° for **3b**), and the Mo–CNR distances, at 2.07 (2) and 2.03

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(29) Due to radiation damage, a progressive decrease in intensity occurred during data collection for **3e**. This and the lack of suitable anisotropic models for the phosphine methyl groups may account for the relatively high final *R* value of 0.093. For this reason, the precise meaning of the structural parameters found for the Mo–CO_2 units in this complex (Tables III and IV) cannot be ascertained. An X-ray determination on a third member of this series is intended with the aim of determining the significance (or otherwise) of the present results.

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(2) Å (**3b** and **3e**), are similar to those found in other Mo(0)–CNR complexes.[35]

Reaction of *cis*-$Mo(N_2)_2(PMe_2Ph)_4$ with CO_2. In 1974, Chatt and co-workers reported briefly on the reactions of CO_2 with some molybdenum dinitrogen complexes.[9] It was found that the complex *cis*-$Mo(N_2)_2(PMe_2Ph)_4$ reacts rapidly with CO_2 to give a new species showing IR bands at 1760, 1510, and 1335 cm^{-1}. When this complex, formulated as $Mo(CO_2)_2(PMe_2Ph)_4$, is dissolved in THF, a new derivative is formed, and this was characterized[9] by X-ray crystallography as the dimeric carbonyl carbonate $[Mo(CO_3)(CO)(PMe_2Ph)_3]_2$.

Because of the dissimilarity of the IR data reported for the supposed CO_2 complex and those obtained for **1** and **3**, we carried out the reaction of *cis*-$Mo(N_2)_2(PMe_2Ph)_4$ with CO_2 under various experimental conditions, including different solvents and pressures of CO_2 (1–5 atm). In our hands, this reaction yields only a red, very crystalline complex, "$Mo(CO_2)_2(PMe_2Ph)_3$", B, with IR bands at the frequencies reported for the supposed CO_2 complex, i.e., 1760, 1510, and 1335 cm^{-1}. It is important to note that the PMe_3 complex $[Mo(CO_3)(CO)(PMe_3)_3]_2$, obtained by reacting *cis*-$Mo(N_2)_2(PMe_3)_4$ with CO_2,[13] shows IR bands at nearly the same frequencies, 1765, 1500, 1335, and 840 cm^{-1}, due to the CO (1765 cm^{-1}) and to the CO_3^{2-} ligands. On the other hand, the reaction of B with neat PMe_2Ph at 50 °C yields, in addition to unreacted B, a red complex C, with IR bands at 1800 and 1600 cm^{-1}, which reconverts rapidly into B upon dissolution in THF. This behavior is very similar to that reported[13] for the complexes $Mo(CO_3)(CO)(PMe_3)_4$ (which shows IR bands at 1810 (CO) and 1600 (CO_3^{2-}) cm^{-1}) and $[Mo(CO_3)(CO)(PMe_3)_3]_2$ and suggests that B and C may be carbonyl carbonate derivatives (eq 3) formed by reductive disproportionation of CO_2 induced by the molybdenum–dinitrogen complex. In spite of our efforts, we have been unable to obtain any evidence indicating the formation of a $Mo–CO_2$ complex in this reaction system.

$$Mo(CO_3)(CO)(PMe_2Ph)_4 \underset{PMe_2Ph}{\overset{THF}{\rightleftharpoons}} {}^1/_2[Mo(CO_3)(CO)(PMe_2Ph)_3]_2 \quad (3)$$

Concluding Remarks

The ranges of transition metal–carbon dioxide complexes have been significantly enlarged with the preparation of the first representatives of a new class of carbon dioxide complexes, which contain two molecules of CO_2 coordinated to the metal atom. The complex *trans*-$Mo(CO_2)_2(PMe_3)_4$, although not structurally characterized, can be conclusively formulated as a bis-CO_2 adduct, based on its characteristic spectroscopic properties and reaction chemistry. The isolation of this complex and its conversion into the series of derivatives **3**, *trans,mer*-$Mo(CO_2)_2(CNR)(PMe_3)_3$, two of which members have been structurally characterized, provide some experimental basis to ascertain dihapto coordination of CO_2 to a transition metal by a combination of IR and ^{13}C NMR spectroscopic studies. All the new compounds prepared in this work, as well as others previously described, show a strong IR absorption in the region 1750–1650 cm^{-1} and a characteristic ^{13}C NMR resonance at 210–195 ppm, due to the dihapto-bonded CO_2 molecules. Due to the limited number of known $M–\eta^2–CO_2$ complexes, the usefulness of this diagnostic criterion for $M–\eta^2–CO_2$ coordination cannot, as yet, be attested. Additional studies on other $M–CO_2$ complexes are, therefore, required to confirm (or otherwise) this hypothesis and to identify, by spectroscopic means, other bonding modes of this molecule.

Complexes **1** and **3** show relatively high thermal stabilities, which we believe are the results of a delicate balance of steric and electronic effects. The importance of these effects is shown by the tendency of **1** to decompose by dissociation of PMe_3 (as found[10] for *trans*-$Mo(C_2H_4)_2(PMe_3)_4$), while complexes **3**, which contain the strong π-acceptor and less steric demanding CNR ligand in substitution of one of the PMe_3 molecules, show no appreciable tendency toward ligand dissociation at room temperature. Our failure to observe adduct formation with the bulkier PMe_2Ph ($\theta = 122°$) is also in agreement with this. Finally, the importance of electronic effects is also shown by the preferred formation of the disproportionation products when the reaction of *cis*-$Mo(N_2)_2(PMe_3)_4$ with CO_2 is carried out in coordinating solvents or in the presence of free PMe_3.[13]

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 Models 577 and 684 spectrophotometers. ^1H NMR spectra were run on a Varian XL-200 spectrometer, and ^{31}P and ^{13}C NMR data were taken on the same instrument and on Bruker WP 60 and WM 250 machines. ^{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 compounds *cis*-$Mo(N_2)_2(PMe_3)_4$[10] and *cis*-$Mo(N_2)_2(PMe_2Ph)_4$[36] were prepared according to the literature procedures. The ligand PMe_3 was obtained by the method of Wolfsberger and Schmidbaur.[37] Isocyanides were from commercial sources or prepared by standard methods.[38]

Synthesis of *trans*-$Mo(CO_2)_2(PMe_3)_4$ (1). The complex *cis*-$Mo(N_2)_2(PMe_3)_4$ (0.68 g, ca. 1.5 mmol) was dissolved in 150 mL of petroleum ether and the solution transferred under N_2 to a 250-mL capacity pressure bottle. After degassing the contents, the vessel was pressurized with CO_2 (5 atm) and left aside over a 15-h period. The resulting flaky-yellow microcrystalline precipitate was filtered off, washed with 10 mL of Et_2O, and dried in vacuo (0.57 g, ca. 80% yield). Although in this form complex **1** is usually analytically and spectroscopically pure, it can be recrystallized from relatively large volumes of THF or toluene in which solvents it is only sparingly soluble. Less-diluted solutions of the bis(dinitrogen) starting material than those indicated above should be avoided in order to reduce contamination with the red disproportionation product $[Mo(CO_3)(CO)(PMe_3)_3]_2$. $^{13}CO_2$-enriched **1**, **1***, was obtained by the same procedure using ^{13}C-enriched CO_2 obtained from Ba^*CO_3 and H_2SO_4. Selected analytical and spectroscopic data for **1** are as follows: IR (Nujol mull) (CO_2 absorptions) 1670 s, 1155 m, and 1100 m cm^{-1}; for **1*** (50% $^{13}CO_2$-enriched) 1670 s, 1630 s*, 1155 m, 1135 m*, 1125 m*, 1100 m, 1090 m*, 1075 m* cm^{-1}. Absorptions marked with asterisks are due to molecules of **1** containing $^{13}CO_2$, and the appearance of six bands in the 1160–1070-cm^{-1} region is probably due to the presence of three isotopomers of **1*** (see text). ^1H NMR (200 MHz, C_6D_6, 55 °C) δ 1.15 (pseudoquintet, $J_{HPapp} = 1.6$ Hz); $^{13}C\{^1H\}$ NMR (62.9 MHz, $C_6D_5CD_3$, room temperature, data for **1***) δ 206.1 (quintet, $^2J_{CP} = 18$ Hz, CO_2). $^{31}P\{^1H\}$ NMR (101.4 MHz, $C_6D_5CD_3$, −60 °C) (AA′BB′system) δ_A 1.88, δ_B −3.25 ($^2J_{AB} = 144.4$, $^2J_{AB'} = -17.8$, $^2J_{AA'} = 14.5$ $^2J_{BB'} = 23.3$ Hz); (24.3 MHz, 60 °C, data for **1***) (1:4:6:4:1: quintet) ($^2J_{PC} = 17.5$ Hz). M_w (cryoscopically, C_6H_6, N_2) calcd for $Mo(CO_2)_2(PMe_3)_4$, 488; found, 410. Microanal. Calcd for $Mo(CO_2)_2(PMe_3)_4$: C, 34.4; H, 7.4; O, 13.1. Found: C, 34.7; H, 7.6; O, 13.1.

Reactions of *trans*-$Mo(CO_2)_2(PMe_3)_4$ (1) with I_2, MeI, and CO. The interaction of these reagents with **1** afforded $MoI_2(PMe_3)_4$ (I_2 and MeI) and *cis*-$Mo(CO)_2(PMe_3)_4$ (with liberation of CO_2) after stirring at room temperature for ca. 0.5–1 h. The evolved CO_2 was analyzed by GC.

Synthesis of $Mo(\eta^2-S_2CO)(CO)_2(PMe_3)_3$. A solution of **1** (0.48 g, ca. 1 mmol) in 50 mL of THF was pressurized at room temperature with 2 atm of COS. The color darkened considerably, and the mixture was stirred for 6 h and then taken to dryness. The residue was dissolved in the minimum amount of THF, filtered, and kept at −30 °C overnight. The resulting well-formed yellow crystals were washed with Et_2O and dried in vacuo (0.24 g, ca. 55% yield). The title compound is best obtained from the reaction of *cis*-$Mo(N_2)_2(PMe_3)_4$ with COS following an analogous procedure: IR (Nujol mull) (CO) 1910, 1820 cm^{-1}; (S_2CO^{2-}) 1690, 1570 cm^{-1}; ^1H NMR (200 MHz, C_6D_6) δ 1.38 (d, $J_{HPapp} = 8.5$ Hz); $^{31}P\{^1H\}$ NMR (81.1 MHz, C_6D_6, room temperature) δ 16.9 (br s, 2 P) and −18.0 (br s, 1 P). M_w (cryoscopically, C_6H_6, N_2) calcd for $Mo(S_2CO)(CO)_2(PMe_3)_3$, 472; found, 406. Anal. Calcd for Mo-

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$(S_2CO)(CO)_2(PMe_3)_3$: C, 30.5; H, 5.7; O, 10.2. Found: C, 30.7; H, 5.8; O, 10.6.

Synthesis of *trans,mer*-$Mo(CO_2)_2(CNR)(PMe_3)_3$ Complexes. To a clear solution of *trans*-$Mo(CO_2)_2(PMe_3)_4$ in toluene (40 mL) was added an excess of the corresponding isocyanide (ca. 3 equiv) via syringe. The resulting mixture was stirred at room temperature for 12 h, and the volatiles were removed under vacuum. Extraction with 40 mL of Et_2O, centrifugation, and cooling at −30 °C furnished the complexes as yellow crystalline materials. This procedure has been applied successfully to the following isocyanides: CNMe, CN-*t*-Bu, CNCy, $CNCH_2Ph$, and CN-*i*-Pr. The yield varied considerably depending on the isocyanide: 80–90% for R = Me, *i*-Pr, and *t*-Bu; 60% for R = Cy and CH_2Ph. In the case of benzyl isocyanide, the use of only the required amount of this reagent makes workup of the reaction considerably easier. $Mo(CO_2)_2(CNMe)(PMe_3)_3$: IR (Nujol mull) ν_{CN} 2140 m, CO_2 absorptions 1660, 1150, and 1100 cm^{-1}; ^1H NMR (60 MHz, C_6D_6) δ 2.49 (s, 3 H, $CN\mathit{Me}$), 1.24 (t, 18 H, 2 $P\mathit{Me}_3$, J_{HPapp} = 3 Hz); and 1.06 (d, 9 H, 1 $P\mathit{Me}_3$, $^2J_{HP}$ = 7 Hz); $^{13}C\{^1H\}$ NMR (62.9 MHz, C_6D_6) δ 201.1 (nonresolved m, $\mathit{C}O_2$), 172.3 (nonresolved m, $\mathit{C}NMe$), 28.3 (br s, $CN\mathit{C}H_3$), 16.49 (d, $P\mathit{Me}_3$ cis, $^1J_{CP}$ = 18 Hz), and 16.18 (t, 2 $P\mathit{Me}_3$ trans, J_{CPapp} = 11 Hz). Anal. Calcd for $Mo(CO_2)_2(CNMe)(PMe_3)_3$: C, 34.4; H, 6.6. Found: C, 34.6; H, 6.7. $Mo(CO_2)_2(CN\text{-}i\text{-}Pr)(PMe_3)_3$: IR (Nujol mull) ν_{CN} 2120 s, CO_2 absorptions 1675 s, 1160 m, and 1100 m cm^{-1}; ^1H NMR δ 3.40 (h, 1 H, $C\mathit{H}Me_2$, $^3J_{HH}$ = 6.5 Hz), 1.27 (t, 18 H, 2 $P\mathit{Me}_3$ trans, J_{HPapp} = 3 Hz), 1.04 (d, 9 H, 1 $P\mathit{Me}_3$, $^2J_{HP}$ = 7 Hz), and 0.99 (d, 6 H, $CH\mathit{Me}_2$, $^3J_{HH}$ = 6.5 Hz); $^{13}C\{^1H\}$ NMR δ 201.4 (nonresolved m, $\mathit{C}O_2$), 47.82 (s, $\mathit{C}HMe_2$) 22.81 (s, $CH\mathit{Me}_2$), 16.52 (d, $P\mathit{Me}_3$ cis, $^1J_{CP}$ = 18 Hz), and 16.11 (t, 2 $P\mathit{Me}_3$ trans, J_{CPapp} = 11 Hz); $^{31}P\{^1H\}$ NMR (101.4 MHz, C_6D_6, room temperature) (approaching an AX_2 system) δ 0.13 (d, 2 P_X trans, $^2J_{P_XP_A}$ = 18 Hz), and 8.82 (br s, 1 P_A cis). Anal. Calcd for $Mo(CO_2)_2(CN\text{-}i\text{-}Pr)(PMe_3)_3$: C, 37.4; H, 7.1. Found: C, 37.3; H, 7.1. $Mo(CO_2)_2(CN\text{-}t\text{-}Bu)(PMe_3)_3$: IR (Nujol mull) ν_{CN} 2100 s, CO_2 absorptions 1680 s, 1155 m, and 1100 m cm^{-1}; ^1H NMR δ 1.40 (t, 18 H, 2 $P\mathit{Me}_3$ trans, J_{HPapp} = 3 Hz), 1.22 (s, 9 H, $C\mathit{Me}_3$), and 1.17 (d, 1 $P\mathit{Me}_3$ cis, $^3J_{HP}$ = 6.5 Hz); $^{13}C\{^1H\}$ NMR (C_6D_6, room temperature, 50% $^{13}CO_2$-enriched sample) δ 201.2 (td, $\mathit{C}O_2$, $^2J_{CP_x}$ = 18, $^2J_{CP_A}$ = 11 Hz), 55.84 (s, $\mathit{C}Me_3$), 29.95 (s, $C\mathit{Me}_3$), 16.47 (d, 1 $P\mathit{Me}_3$ cis, $^1J_{CP}$ = 18 Hz), and 16.12 (t, 2 $P\mathit{Me}_3$ trans, J_{CPapp} = 11 Hz); $^{31}P\{^1H\}$ NMR (C_6D_6, 45 °C) (AX_2 system) δ 0.43 (d, 2 P_X trans, $^2J_{P_xP_A}$ = 19 Hz), and −8.40 (t, P_A, this signal broadens at room temperature). Anal. Calcd for $Mo(CO_2)_2(CN\text{-}t\text{-}Bu)(PMe_3)_3$: C, 38.8; H, 7.3. Found: C, 38.9; H, 7.2. $Mo(CO_2)_2(CNCy)(PMe_3)_3$: IR (Nujol mull) ν_{CN} 2100 s, CO_2 absorptions 1665 s, 1150 s, and 1100 s cm^{-1}; ^1H NMR δ 3.31 and 1.53 (br, $C_6\mathit{H}_{11}$), 1.36 (t, 18 Hz, 2 $P\mathit{Me}_3$ trans, J_{HPapp} = 3 Hz), and 1.10 (d, 9 H, 1 $P\mathit{Me}_3$ cis, $^2J_{HP}$ = 6.5 Hz); $^{13}C\{^1H\}$ NMR (33% $^{13}CO_2$-enriched sample) δ 201.4 (td, $\mathit{C}O_2$, $^2J_{CP_X}$ = 18, $^2J_{CP_A}$ = 11 Hz), 53.74 (s, $CN{-}\mathit{C}{\equiv}$), 32.53, 24.73, and 22.96 (s, other cyclohexyl carbons), 16.54 (d, 1 $P\mathit{Me}_3$ cis, $^1J_{CP}$ = 18 Hz), and 16.16 (t, 2 $P\mathit{Me}_3$ trans, J_{CPapp} = 11 Hz); $^{31}P\{^1H\}$ NMR (C_6D_6, room temperature) (approaching an AX_2 system) δ 0.99 (d, 2 P_X, $^2J_{P_XP_A}$ = 18 Hz (in the spectrum of a 33% $^{13}CO_2$-enriched sample, a superimposed triplet can be observed) $^2J_{P_XP_A}$ = $^2J_{P_XC}$ = 18 Hz), and −7.85 (br, P_X). Anal. Calcd for $Mo(CO_2)_2(CNCy)(PMe_3)_3$: C, 41.5; H, 7.3. Found: C, 41.7; H, 7.4. $Mo(CO_2)_2(CNCH_2Ph)(PMe_3)_3$: IR (Nujol mull) ν_{CN} 2090 s, CO_2 absorptions 1670 s, 1150 m, and 1100 m cm^{-1}; ^1H NMR δ 7.46–7.05 (m, 5 H, $CH_2C_6\mathit{H}_5$), 4.28 (s, 2 H, $C\mathit{H}_2C_6H_5$), 1.28 (t, 18 H, 2 $P\mathit{Me}_3$ trans, J_{HPapp} = 3 Hz), and 1.08 (d, 9 H, 1 $P\mathit{Me}_3$ cis, $^2J_{HP}$ = 6.5 Hz); $^{13}C\{^1H\}$ NMR δ 201.8 (nonresolved m, $\mathit{C}O_2$), and 175.2 (nonresolved m, $\mathit{C}NCH_2Ph$); $^{31}P\{^1H\}$ NMR (C_6D_6, 45 °C) δ 0.85 (d, 2 P_X, $J_{P_XP_A}$ = 20 Hz), and −10.10 (t, P_A). Anal. Calcd for $Mo(CO_2)_2(CNCH_2Ph)(PMe_3)_3$: C, 43.1; H, 6.4. Found: C, 43.2; H, 6.6.

Reaction of *cis*-$Mo(N_2)_2(PMe_2Ph)_4$ with CO_2. Although the interaction of CO_2 with this dinitrogen complex has been studied under a variety of experimental conditions, including different solvents, pressures of CO_2, and variable concentrations of the dinitrogen complex, only one molybdenum-containing product of composition, $[Mo(CO_3)(CO)(PMe_2Ph)_3]_2$,[9] has been isolated. Two representative experiments are described below.

(A) A stirred solution of *cis*-$Mo(N_2)_2(PMe_2Ph)_4$ (0.5 g, ca. 0.9 mmol) in 20 mL of THF was exposed to 1 atm of CO_2. The initial yellow color of the reaction mixture rapidly (1–2 min) turned red. Monitoring the course of the reaction by IR spectroscopy showed this to be essentially complete after 1 h. Reduction of the volume in vacuo and cooling at −30 °C overnight furnished small well-formed red crystals, which were filtered, washed with a small amount (ca. 5–10 mL) of Et_2O, and dried in vacuo: yield, 0.4 g; IR (Nujol mull) ν_{CO} 1760, CO_3^{2-} absorptions 1510 and 1335 cm^{-1}. Anal. Calcd for $[Mo(CO_3)(CO)(PMe_2Ph)_3]_2$: C, 52.2; H, 5.5. Found: C, 53.3; H, 5.9.

(B) *cis*-$Mo(N_2)_2(PMe_2Ph)_4$ (0.5 g) was dissolved in a mixture of 65 mL of Et_2O and 10 mL of THF. The resulting solution was transferred to a pressure bottle, pressurized with CO_2 (5 atm), and left aside for 24 h. The resulting red crystals were filtered, washed with Et_2O, and dried in vacuo: yield, 0.4 g. The IR spectrum of this material is indistinguishable from that of the compound obtained by method A.

Table V. Crystal Data for Compounds **2**, **3b**, and **3e**

	2	**3b**	**3e**
formula	$C_{12}H_{27}MoP_3S_2O_3$	$C_{15}H_{34}MoNO_4P_3$	$C_{19}H_{34}MoNO_4P_3$
fw	472.33	481.29	529.34
cell dimensions			
a, Å	14.003 (2)	29.47 (3)	11.563 (8)
b, Å	9.767 (2)	13.01 (1)	11.792 (7)
c, Å	15.127 (2)	16.77 (1)	18.57 (1)
β, deg		132.41 (3)	90.42 (4)
V, Å^3	2068.9 (6)	4747 (7)	2532 (2)
system	orthorhombic	monoclinic	monoclinic
space group	$Pna2_1$	$C2/c$	$P2_1/c$
Z	4	8	4
d_{calcd}, g·cm^{-3}	1.52	1.35	1.39
μ (Mo Kα), cm^{-1}	10.46	7.54	7.13

Table VI. Atomic Coordinates for $Mo(S_2CO)(CO)_2(PMe_3)_3$

atom	*X*/*A*	*Y*/*B*	*Z*/*C*
M0	0.2074 (0)	0.1753 (1)	0.0000 (0)
P1	0.1746 (6)	0.2828 (7)	0.1453 (4)
C11	0.1290 (11)	0.4610 (16)	0.1359 (11)
C12	0.2684 (10)	0.2986 (15)	0.2206 (10)
C13	0.0798 (10)	0.2013 (15)	0.2189 (10)
P2	0.1202 (1e	−0.0619 (2)	−0.0014 (6)
C21	0.0318 (11)	−0.0871 (16)	0.0957 (11)
C22	0.1895 (6)	−0.2213 (10)	0.0140 (9)
C23	0.0487 (13e	−0.1040 (18)	−0.0894 (12)
P3	0.1756 (5)	0.2856 (7)	−0.1455 (4)
C31	0.1230 (10)	0.1914 (14)	−0.2321 (10)
C32	0.1103 (10)	0.4439 (15)	−0.1486 (10)
C33	0.2928 (10)	0.3363 (14)	−0.2034 (9)
S1	0.3233 (6)	0.0375 (7)	−0.0979 (4)
S2	0.3250 (5)	0.0417 (7)	0.0936 (4)
C1	0.3784 (6)	−0.0258 (8)	0.0038 (26)
O1	0.4473 (5)	−0.1031 (7)	−0.0065 (20)
C2	0.0719 (6)	0.2202 (8)	−0.0118 (8)
O2	−0.0093 (4)	0.2384 (7)	−0.0085 (20)
C3	0.2806 (5e	0.3486 (8	−0.0011 (24)
O3	0.3193 (4)	0.4539 (7)	−0.0020 (21)
H111	0.071 (0)	0.443 (0)	0.120 (0)
H112	0.178 (0e	0.510 (0)	0.108 (0)
H113	0.101 (0)	0.487 (0)	0.210 (0)
H121	0.333 (0)	0.249 (0)	0.210 (0)
H122	0.282 (0)	0.396 (0)	0.230 (0)
H123	0.244 (0)	0.258 (0)	0.280 (0)
H131	0.087 (0)	0.114 (0)	0.216 (0)
H132	0.086 (0)	0.263 (0)	0.269 (0)
H133	0.032 (0)	0.206 (0)	0.192 (0)
H211	0.018 (0)	−0.187 (0)	0.076 (0)
H212	0.000 (0)	−0.027 (0)	0.083 (0)
H213	0.073 (0)	−0.088 (0)	0.140 (0)
H221	0.140 (0)	−0.306 (0)	−0.003 (0)
H222	0.207 (0)	−0.214 (0)	0.064 (0)
H223	0.209 (0)	−0.215 (0)	−0.067 (0)
H231	0.078 (0)	−0.080 (0)	−0.154 (0)
H232	0.000 (0)	−0.028 (0)	−0.088 (0)
H233	0.019 (0)	−0.187 (0)	−0.073 (0)
H311	0.177 (0)	0.170 (0)	−0.276 (0)
H312	0.098 (0)	0.106 (0)	−0.208 (0)
H313	0.089 (0)	0.281 (0)	−0.235 (0)
H321	0.078 (0)	0.455 (0)	−0.090 (0)
H322	0.157 (0)	0.519 (0)	−0.158 (0)
H323	0.082 (0)	0.390 (0)	−0.199 (0)
H331	0.355 (0)	0.320 (0)	−0.162 (0)
H332	0.299 (0)	0.276 (0)	−0.257 (0)
H333	0.255 (0)	0.425 (0)	−0.206 (0)

The reaction of this complex with neat PMe_2Ph at 40–50 °C gave a red solid which has been shown by IR spectroscopy to contain unreacted starting material and a new compound displaying IR absorptions at 1800

Table VII. Atomic Coordinates for $Mo(CO_2)_2(i\text{-}PrNC)(PMe_3)_3$

atom	X/A	Y/B	Z/C
H22	0.173 00 (0)	0.412 50 (0)	−0.042 40 (0)
M0	0.124 60 (4)	0.202 30 (6)	0.152 40 (6)
O11	0.075 10 (33)	0.060 00 (50)	0.085 50 (57)
C10	0.079 90 (51)	0.099 00 (78)	0.022 80 (87)
O12	0.065 00 (43)	0.069 50 (68)	−0.061 50 (63)
O21	0.194 30 (34)	0.311 30 (59)	0.267 70 (59)
C20	0.142 80 (56)	0.354 30 (81)	0.211 90 (92)
O22	0.126 40 (44)	0.441 60 (62)	0.209 20 (79)
C1	0.132 20 (52)	0.272 10 (81)	0.050 90 (92)
N1	0.135 40 (61)	0.309 00 (91)	−0.006 70 (93)
C2	0.136 30 (101)	0.357 40 (181)	−0.086 70 (178)
C3	0.153 30 (90)	0.282 90 (160)	−0.125 50 (160)
C4	0.105 30 (96)	0.448 70 (170)	−0.124 00 (167)
P1	0.019 00 (13)	0.274 20 (20)	0.038 80 (24)
C11	−0.005 90 (63)	0.343 80 (107)	0.098 10 (110)
C12	0.001 20 (63)	0.369 70 (107)	−0.058 80 (110)
C13	−0.043 40 (70)	0.181 80 (121)	−0.047 60 (123)
P2	0.215 60 (14)	0.092 00 (24)	0.220 50 (24)
C21	0.290 60 (84)	0.130 40 (147)	0.344 10 (149)
C22	0.231 70 (79)	0.088 70 (135)	0.133 90 (117)
C23	0.210 90 (81)	−0.041 40 (140)	0.239 10 (142)
P3	0.129 80 (16)	0.147 10 (26)	0.304 20 (25)
C31	0.120 30 (90)	0.247 40 (158)	0.368 20 (158)
C32	0.201 90 (92)	0.098 90 (158)	0.428 40 (161)
C33	0.077 30 (106)	0.056 30 (183)	0.271 60 (185)
H131	−0.047 00 (0)	0.134 10 (0)	−0.004 30 (0)
H132	−0.084 10 (0)	0.215 80 (0)	−0.104 40 (0)
H133	−0.030 00 (0)	0.142 60 (0)	−0.080 00 (0)
H121	−0.043 80 (0)	0.386 60 (0)	−0.114 90 (0)
H122	0.024 90 (0)	0.435 40 (0)	−0.023 80 (0)
H123	0.014 80 (0)	0.332 30 (0)	−0.092 20 (0)
H111	0.17 50 (0)	0.409 70 (0)	0.134 60 (0)
H112	−0.051 20 (0)	0.360 80 (0)	0.043 50 (0)
H113	0.003 50 (0)	0.292 60 (0)	0.152 00 (0)
H231	0.243 40 (0)	−0.082 80 (0)	0.249 70 (0)
H232	0.213 90 (0)	−0.053 90 (0)	0.301 40 (0)
H233	0.168 90 (0)	−0.063 60 (0)	0.169 50 (0)
H221	0.244 90 (0)	0.156 70 (0)	0.127 60 (0)
H222	0.264 20 (0)	0.035 80 (0)	0.158 20 (0)
H223	0.190 50 (0)	0.067 40 (0)	0.064 50 (0)
H211	0.324 00 (0)	0.077 80 (0)	0.371 80 (0)
H212	0.304 70 (0)	0.198 60 (0)	0.341 20 (0)
H213	0.282 90 (0)	0.132 20 (0)	0.394 80 (0)
H321	0.236 70 (0)	0.151 60 (0)	0.466 90 (0)
H322	0.200 00 (0)	0.071 90 (0)	0.481 40 (0)
H323	0.208 30 (0)	0.043 40 (0)	0.395 00 (0)
H331	0.087 70 (0)	0.026 20 (0)	0.337 70 (0)
H332	0.034 80 (0)	0.079 70 (0)	0.219 90 (0)
H333	0.082 70 (0)	−0.003 30 (0)	0.236 70 (0)
H311	0.117 30 (0)	0.223 10 (0)	0.420 20 (0)
H312	0.154 00 (0)	0.302 80 (0)	0.405 70 (0)
H313	0.080 50 (0)	0.276 50 (0)	0.300 10 (0)
H41	0.121 20 (0)	0.489 80 (0,	−0.151 30 (0)
H42	0.061 70 (0)	0.423 70 (0)	−0.191 90 (0)
H43	0.094 10 (0)	0.503 60 (0)	−0.097 40 (0)
H31	0.111 60 (0)	0.253 40 (0)	−0.192 10 (0)
H32	0.171 10 (0)	0.319 50 (0)	−0.151 50 (0)
H33	0.178 90 (0)	0.215 60 (0)	−0.095 80 (0)

and 1600 cm^{-1}. Upon dissolution in THF and evaporation of the solvent in vacuo, the starting $[Mo(CO_3)(CO)(PMe_2Ph)_3]_2$ was obtained as the only observable product.

X-ray Structure Determinations. A summary of the fundamental crystal data for the three compounds **2**, **3b**, and **3e** is given in Table V. Single crystals of the CO_2 adducts are difficult to obtain, and only very freshly prepared samples diffract properly enough as to permit the X-ray analysis. Furthermore, **3e** decomposes quickly upon X-ray radiation. The chosen crystals of the three compounds were mounted under nitrogen in glass capillaries and the data collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) using $\omega - 2\theta$ scans. The scattering factors for neutral atoms and anomalous dispersion corrections for Mo, P, and S were taken from ref 39. Most of the calculations were carried out with the X-RAY 80 system.[40]

Table VIII. Atomic Coordinates for $Mo(CO_2)_2(PMe_3)_3(CNCH_2Ph)$

atom	X/A	Y/B	Z/C
M0	0.772 00 (12)	0.233 50 (11)	0.248 40 (10)
P1	0.878 80 (45)	0.313 10 (43)	0.355 40 (36)
C11	1.023 80 (196)	0.366 30 (205)	0.339 80 (148)
C12	0.812 00 (232)	0.422 00 (246)	0.409 50 (178)
C13	0.908 10 (203)	0.207 90 (226)	0.424 70 (164)
P2	0.625 20 (41)	0.145 10 (46)	0.166 90 (38)
C21	0.475 20 (181)	0.178 20 (186)	0.186 80 (143)
C22	0.627 30 (204)	−0.008 50 (211)	0.168 70 (155)
C23	0.634 10 (215)	0.173 30 (226)	0.070 40 (166)
P3	0.766 10 (44)	0.422 70 (42)	0.180 20 (39)
C31	0.621 20 (188)	0.467 50 (193)	0.161 00 (144)
C32	0.819 00 (210)	0.553 80 (227)	0.221 20 (164)
C33	0.842 90 (223)	0.425 80 (232)	0.097 30 (169)
C10	0.643 80 (158)	0.211 00 (121)	0.320 60 (120)
O11	0.621 50 (86)	0.306 70 (97)	0.295 50 (78)
O12	0.591 70 (108)	0.157 80 (108)	0.370 00 (91)
C20	0.876 50 (147)	0.172 00 (134)	0.170 80 (127)
O21	0.947 20 (80)	0.215 60 (102)	0.209 70 (74)
O22	0.892 50 (118)	0.126 60 (123)	0.108 90 (89)
C1	0.799 70 (127)	0.076 00 (139)	0.289 10 (128)
N1	0.817 20 (114)	−0.017 00 (125)	0.313 90 (98)
C2	0.822 70 (182)	−0.132 30 (139)	0.335 00 (144)
C3	0.764 10 (135)	−0.161 30 (135)	0.404 90 (118)
C4	0.805 10 (157)	0.259 20 (146)	0.438 40 (132)
C5	0.748 90 (182)	−0.294 00 (178)	0.500 60 (135)
C6	0.657 10 (178)	−0.235 20 (195)	0.524 90 (130)
C7	0.619 80 (155)	−0.136 50 (157)	0.491 30 (126)
C8	0.674 80 (133)	−0.101 20 (142)	0.431 40 (123)
H4	0.875 00 (0)	−0.305 40 (0)	0.417 50 (0)
H5	0.784 40 (0)	−0.359 90 (0)	0.529 70 (0)
H6	0.611 70 (0)	−0.271 00 (0)	0.569 40 (0)
H7	0.551 30 (0)	−0.090 50 (0)	0.511 60 (0)
H8	0.645 30 (0)	−0.035 30 (0)	0.403 30 (0)
H21	0.788 20 (0)	−0.181 30 (0)	0.294 50 (0)
H22	0.908 70 (0)	−0.154 10 (0)	0.337 60 (0)
H111	1.023 40 (0)	0.440 60 (0)	0.312 30 (0)
H112	1.070 40 (0)	0.375 70 (0)	0.384 40 (0)
H113	1.063 60 (0)	0.307 10 (0)	0.307 50 (0)
H121	0.856 30 (0)	0.428 80 (0)	0.457 00 (0)
H122	0.809 30 (0)	0.493 70 (0)	0.384 80 (0)
H123	0.732 50 (0)	0.390 90 (0)	0.420 30 (0)
H131	0.957 70 (0)	0.144 80 (0)	0.407 50 (0)
H132	0.941 70 (0)	0.241 30 (0)	0.469 70 (0)
H133	0.826 40 (0)	0.178 10 (0)	0.435 10 (0)
H211	0.419 90 (0)	0.146 50 (0)	0.149 60 (0)
H212	0.450 90 (0)	0.151 40 (0)	0.235 50 (0)
H213	0.472 00 (0)	0.264 30 (0)	0.185 00 (0)
H221	0.604 90 (0)	−0.040 30 (0)	0.219 00 (0)
H222	0.573 90 (0)	−0.045 10 (0)	0.133 10 (0)
H223	0.709 60 (0)	−0.030 90 (0)	0.159 50 (0)
H231	0.577 90 (0)	0.124 10 (0)	0.041 40 (0)
H232	0.614 80 (0)	0.255 20 (0)	0.058 30 (0)
H233	0.714 70 (0)	0.155 10 (0)	0.058 40 (0)
H311	0.575 10 (0)	0.481 30 (0)	0.206 20 (0)
H312	0.615 20 (0)	0.533 70 (0)	0.128 90 (0)
H313	0.591 30 (0)	0.395 50 (0)	0.136 20 (0)
H321	0.814 30 (0)	0.622 60 (0)	0.271 30 (0)
H322	0.774 20 (0)	0.570 20 (0)	0.236 50 (0)
H323	0.899 60 (0)	0.531 00 (0)	0.236 50 (0)
H331	0.809 20 (0)	0.370 00 (0)	0.061 70 (0)
H332	0.844 80 (0)	0.502 20 (0)	0.075 70 (0)
H333	0.927 00 (0)	0.400 30 (0)	0.106 90 (0)

Compound 2. A total of 2565 reflections was measured in one octant out to 2θ = 56° from a yellow spherical crystal. The three periodically monitored standard reflections exhibited random variation in intensity within ±5%. The data were corrected for Lorentz and polarization effects, and 1939 reflections were considered observed ($I > 3\sigma(I)$). The structure was solved by Patterson and Fourier techniques, and an empirical absorption correction[41] was applied at the end of the isotropic refinement. Subsequent full matrix least-squares isotropic refinement cycles for the phosphine carbon atoms and anisotropic for the rest led to

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(39) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, pp 72–98.

(40) Stewart, J. M. "The XRAY 80 System"; Computer Science Center, University of Maryland: College Park, 1985.

(41) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *A39*, 158.

$R = 0.044$. Successive Fourier synthesis calculated with reflections having $\sin \theta/\lambda < 0.5$ Å^{-1} showed 19 of the 27 H atoms, the remainder being geometrically placed. The final refinement cycles, with the H atoms held invariant, yielded a final R value of 0.038 ($R_W = 0.044$). Unit weights were used, and no trend in ΔF vs. F_o or $\sin \theta/\lambda$ was observed.

Compound 3b. A yellow-orange, block-shaped crystal was used, and 4163 unique reflections were measured in a quadrant within the θ range $0 \leq \theta \leq 25$, of which 3493 were considered observed [$F_o^2 \geq 3\sigma(F_o^2)$] after data reduction (Lorentz and polarization but no absorptions corrections were made) and used in the subsequent calculations. The Patterson map permitted the location of the Mo atom, and successive F_{obsd} Fourier synthesis provided the coordinates of the remaining non-H atoms. The refinement was carried out by full-matrix least-squares procedures (isotropic for the isopropyl group and phosphine carbon atoms; anisotropic for the rest) using unit weights as no bias on ΔF was appreciated. The final R value was 0.076 ($R_W = 0.080$).

Compound 3e. A yellow irregular-shaped crystal was studied, and 4044 unique reflections from it were measured up to $\theta = 28°$. Due to radiation damage, a progressive decrease in intensity occurred as revealed for the three periodically checked standard reflections. To minimize the effect, a time limit of 45 s was adopted for the final scan of a reflecting position. The data were scaled from the standard intensities variations (ca. 30% at the end of the collecting process) and corrected for Lorentz, polarization, and absorption[41] effects; 1907 reflections were considered observed ($I > 3\sigma(I)$) and used for structure solution and refinement. Three-dimensional Patterson and Fourier syntheses allowed location for all non-H atoms, and subsequent full-matrix least-squares refinement, using F's and unit weights, keeping the methyl carbon atoms isotropic, led to $R = 0.096$. The H atoms were included in the refinement with fixed contributions at their calculated positions.

In order to prevent bias on ΔF vs. F_o or $\sin \theta/\lambda$, the last steps of the refinement were carried out with weights[42] $w = 1/(a + b|F_o|)^2$, where $a = 5.91$, $b = -0.09$, if $|F_o| < 32$, and $a = 1.31$, $\beta = 0.06$, if $|F_o| \geq 32$. The final R values were $R = 0.093$ and $R_W = 0.093$.

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Registry No. 1, 89711-40-0; **1**-$^{13}C_2$, 100790-42-9; **2**, 100790-43-0; **3a**, 94985-87-2; **3b**, 94985-86-1; **3c**, 94985-88-3; **3d**, 100790-44-1; **3e**, 100790-45-2; *cis*-$Mo(N_2)_2(PMe_3)_4$, 82044-78-8; $MoI_2(PMe_3)_4$, 82456-13-1; *cis*-$Mo(CO)_2(PMe_3)_4$, 30513-06-5; *cis*-$Mo(N_2)_2(PMe_2Ph)_4$, 32457-67-3; $[Mo(CO_3)(CO)(PMePh)_3]_2$, 55913-76-3.

Supplementary Material Available: Thermal parameters and observed and calculated structure factor amplitudes for Mo(S_2CO)$(CO)_2(PMe_3)_3$, $Mo(CO_2)_2$(CN-*i*-Pr)$(PMe_3)_3$, and Mo$(CO_2)_2(CNCH_2Ph)(PMe_3)_3$ (Tables A–F) (75 pages). Ordering information is given on any current masthead page.

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Molecular Hydrogen Complexes of the Transition Metals. 3.[1] Preparation, Structure, and Reactivity of $W(CO)_3(PCy_3)_2$ and $W(CO)_3(P(i\text{-}Pr)_3)_2$, η^2-H_2 Complex Precursors Exhibiting M···H—C Interaction

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Abstract: The synthesis, reactivity, and molecular structures of coordinatively and electronically unsaturated complexes $M(CO)_3(PR_3)_2$ [M = Mo, W; R = Cy, *i*-Pr] are described. Ligands that bind reversibly to $W(CO)_3(PCy_3)_2$ include H_2, N_2, C_2H_4, H_2O, ROH, and thiophene; irreversibly bound ligands are MeCN, pyridine, NH_3, $CyNH_2$, and PR_3. The structures of $W(CO)_3(PCy_3)_2$ and $W(CO)_3(P(i\text{-}Pr)_3)_2$ involve incipient intramolecular oxidative addition of a distal phosphine C–H bond to the metal. The three-center M···H—C interaction in $W(CO)_3(PCy_3)_2$ has W–H(11a)–C(11) = 127.6°, W–C(11) = 2.945 (6) Å, and W–H(11a) $\cong$ 2.27 Å. Crystal data for $W(CO)_3(PCy_3)_2$ are the following: space group $P\bar{1}$, $a = 10.300$ (1) Å, $b = 12.675$ (2) Å, $c = 15.473$ (1) Å, $\alpha = 91.44$ (1)°, $\beta = 90.37$ (1)°, $\gamma = 103.99$ (1)°, $Z = 2$, ρ(calcd) = 1.34 g cm^{-3}, $R = 0.025$, 6211 reflections. Crystal data for $W(CO)_3(P\text{-}i\text{-}Pr_3)_2$ are the following: $P2_1/m$, $a = 8.425$ (1) Å, $b = 13.375$ (2) Å, $c = 12.039$ (2) Å, $\beta = 109.58$ (1)°, $Z = 2$, ρ(calcd) = 1.53 g cm^{-3}, $R = 0.034$, 2212 reflections. Since these molecules add dihydrogen to form stable η^2-H_2 complexes, they afford an unprecedented opportunity to observe both H–H and C–H bond activation at a single metal center.

Recently we reported the preparation and complete characterization of complexes in which a dihydrogen *molecule* is present as an η^2-bound ligand.[1] These species, of composition M$(CO)_3(PR_3)_2(\eta^2$-$H_2)$ [M = Mo, W; R = cyclohexyl, isopropyl], were prepared at room temperature by addition of H_2 to solutions containing the formally five-coordinate, 16-electron complexes, $M(CO)_3(PR_3)_2$. The synthesis of the latter compounds from available reagents was reported in preliminary form several years ago.[2] We now report in full the properties and reactions of these unusual formally coordinatively and electronically unsaturated complexes, including full three-dimensional single-crystal X-ray diffraction analyses of $W(CO)_3(PCy_3)_2$ and $W(CO)_3(P(i\text{-}Pr)_3)_2$. The results of these investigations show that the stable form of these compounds involves incipient intramolecular oxidative addition of a distal phosphine C–H bond to the metal. The complexes thus join a rapidly expanding class of molecules possessing three-center M···H—C ("agostic") interactions,[3] although they present rare examples in which this type of interaction occurs in

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