PAPER

NJC
www.rsc.org/njc

# Novel carbon dioxide and carbonyl carbonate complexes of molybdenum. The X-ray structures of *trans*-$[Mo(CO_2)_2\{HN(CH_2CH_2PMe_2)_2\}(PMe_3)]$ and $[Mo_3(\mu_2\text{-}CO_3)(\mu_2\text{-}O)_2(O)_2(CO)_2(H_2O)(PMe_3)_6]\cdot H_2O$

**Leopoldo Contreras,[a] Margarita Paneque,[a] Murielle Sellin,[a] Ernesto Carmona,*[a] Pedro J. Pérez,[b] Enrique Gutiérrez-Puebla,[c] Angeles Monge[c] and Caridad Ruiz[c]**

[a] *Departamento de Química Inorgánica, Instituto de Investigaciones Químicas, Universidad de Sevilla–Consejo Superior de Investigaciones Científicas, Avda. Américo Vespucio s/n, Isla de la Cartuja, E-41092 Sevilla, Spain. E-mail: guzman@us.es*
[b] *Departamento de Química y Ciencia de los Materiales, Universidad de Huelva, Campus de El Carmen s/n, E-21007 Huelva, Spain. E-mail: perez@dqcm.uhu.es*
[c] *Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas, Campus de Cantoblanco, E-28049 Madrid, Spain*

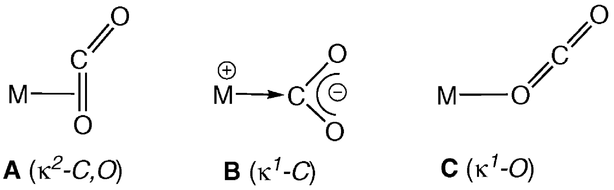
***Received (in Montpellier, France) 19th June 2004, Accepted 10th November 2004***
***First published as an Advance Article on the web 13th December 2004***

A new bis(carbon dioxide) adduct of molybdenum containing the tridentate, bis(phosphine) ligand, $HN(CH_2CH_2PMe_2)_2$ ($NP_2$), in a *mer* conformation has been synthesized and structurally characterized. Its carbonyl carbonate isomer $[Mo(CO_3)(CO)(NP_2)(PMe_3)]$ has also been prepared. In addition, the reactivity of the complex $[Mo(CO_3)(CO)(PMe_3)_4]$ toward CO has been studied, a transformation that has led to the formation of the dicarbonyl complex $[Mo(CO_3)(CO)_2(PMe_3)_3]$. This complex liberates $CO_2$ upon heating under a carbon monoxide atmosphere by means of a CO–$CO_3$ conproportionation reaction. The new trinuclear complex $[Mo_3(\mu_2\text{-}CO_3)(\mu_2\text{-}O)_2(O)_2(CO)_2(H_2O)(PMe_3)_6]\cdot H_2O$, resulting from the interaction of $[Mo(CO_3)(CO)(PMe_3)_4]$ and water, has been isolated and structurally characterized.

## Introduction

The serious environmental problems associated with global warming have stimulated further academic and industrial research into carbon dioxide, as this substance is a major component of the greenhouse gases.[1] In addition, there is growing interest in the use of $CO_2$ as a C1 source for chemicals and fuels, as well as in a variety of technological applications.[2] A key step in the chemical, photochemical and electrochemical transformations of $CO_2$ is the formation of a M–$CO_2$ complex, since coordination to a metal centre activates this rather unreactive molecule toward a number of chemical reactions. It is noteworthy that despite the importance of the M–$CO_2$ functionality, the number of structurally characterized mononuclear complexes is still limited.

Of the three coordination modes that may be envisaged for a M–$CO_2$ unit, namely the side-on $\kappa^2$-*C,O* (Scheme 1, structure **A**) and the end-on $\kappa^1$-*C* or $\kappa^1$-*O* (**B** and **C**, respectively), only **A** and **B** have been authenticated by X-ray crystallography. $\kappa^1$-*C* coordination has been found in $[RhCl(CO_2)(diars)]$[3a] and $[Ru(CO_2)(CO)(bipy)_2]\cdot 3H_2O$,[3b] whereas side-on binding (**A**) has been demonstrated in complexes of both the early and the late transition elements.[4,5] All these compounds contain a single M–$CO_2$ unit, with the only exception of some Mo complexes prepared by our group some years ago, which possess a *trans*-$Mo(CO_2)_2$ functionality.[5]



**Scheme 1** Coordination modes of carbon dioxide.

One of the reactions a coordinated molecule of $CO_2$ may undergo is reduction to CO by means of oxygen atom transfer to another substrate. The latter can be an oxophilic metal[6] or a phosphine ligand[7] (or other readily oxidized ligand). But it is also possible for $CO_2$ to act as its own oxygen sink, giving rise to CO and $CO_3^{2-}$ [eqn. (1)] in a reaction called reductive disproportionation of $CO_2$:[7,8]

$$2\ CO_2 + 2\ e^- \rightarrow CO_3^{2-} + CO \qquad (1)$$

Most often this is an irreversible process that leads to carbonato complexes, nevertheless in a few instances, a metal-carbonate complex has been shown to react with CO to produce $CO_2$.[9] This is the reverse of eqn. (1), that is the oxidative conproportionation of carbon dioxide.

Following previous work on the generation of Mo–$CO_2$ adducts[5] and Mo carbonyl carbonate complexes,[8] we would like to report new findings in this area that include the structural characterization by X-ray methods of the bis($CO_2$) adduct, *trans*-$[Mo(CO_2)_2(NP_2)(PMe_3)]$ (**1**), which contains the tridentate ligand $HN(CH_2CH_2PMe_2)_2$ ($NP_2$). An X-ray study on the trinuclear, mixed-valence Mo(II)–Mo(VI) complex of composition $[Mo_3(\mu_2\text{-}CO_3)(\mu_2\text{-}O)_2(O)_2(CO)_2(H_2O)(PMe_3)_6]\cdot H_2O$ (**4**) is also reported.

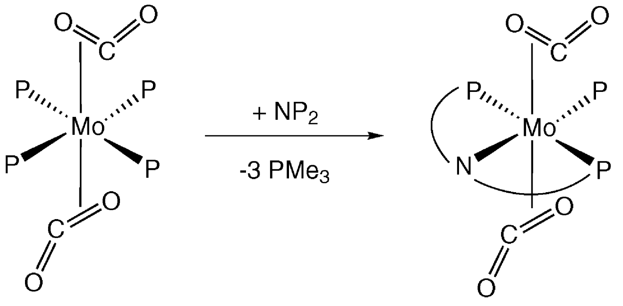
DOI: 10.1039/b409385b

## Results and discussion

### Synthesis and molecular structure of *trans*-[Mo(CO$_2$)$_2$(NP$_2$)(PMe$_3$)] (1)

We have shown earlier that the Mo(0) compound *trans*-[Mo(CO$_2$)$_2$(PMe$_3$)$_4$] exhibits a characteristic substitution chemistry that allows stepwise replacement of the labile PMe$_3$ groups, without alteration of the *trans*-Mo(CO$_2$)$_2$ linkage.[5] During formation of compounds of composition *trans*-[Mo(CO$_2$)$_2$(PMe$_3$)$_3$(CNR)], *trans*-[Mo(CO$_2$)$_2$(PMe$_3$)$_2$(Me$_2$PCH$_2$CH$_2$PMe$_2$)], and others,[5b] the two CO$_2$ ligands remain staggered with respect to one another and eclipse the *trans*-L–Mo–L′ vectors of the plane perpendicular to the *trans*-Mo(CO$_2$)$_2$ bond axis. This conformation, found to be the most favourable by *ab initio* calculations with the model compound *trans*-[Mo(CO$_2$)$_2$(PH$_3$)$_4$], maximizes the Mo(CO$_2$)$_2$ bonding interaction.[10]

As previous substitution chemistry involved either mono- or bidentate ligands,[5] we wondered if the use of a tridentate ligand could force the two molecules of CO$_2$ into a *cis* geometry, and perhaps induce their subsequent coupling to give the corresponding head-to-tail or head-to-head dimers.[11] Edwards' HN(CH$_2$CH$_2$PMe$_2$)$_2$ (NP$_2$) was synthesized[12] and used for this purpose. Nonetheless, and despite the flexibility of this and related ligands that allows them to coordinate to the metal either in *facial* or *meridional* forms,[13] the addition of NP$_2$ to solutions of *trans*-[Mo(CO$_2$)$_2$(PMe$_3$)$_4$] gives the *trans*-Mo(CO$_2$)$_2$ compound **1** [eqn. (2)] as the only detectable product:



**1**

(2)

Monitoring of the reaction by $^{31}$P{$^1$H} NMR spectroscopy shows exclusive appearance of signals due to an AMX spin system and to free PMe$_3$. From the resulting solutions, compound **1** can be isolated as a yellow crystalline material in *ca.* 70% yield. **1** is soluble in aromatic hydrocarbons, tetrahydrofuran, methanol and other common aromatic solvents. Solutions in methanol exhibit an orange colour, perhaps due to extensive hydrogen bonding involving molecules of the solvent.

The IR spectrum of **1** shows bands at 1660, 1155 and 1100 cm$^{-1}$, which can be assigned to vibrations arising from the coordinated molecules of CO$_2$ by comparison with the spectrum of **1*** (*ca.* 30% $^{13}$CO$_2$-enriched). These absorptions have strikingly similar energies to those of the starting material and of other *trans*-Mo(CO$_2$)$_2$ adducts.[5] In the $^1$H NMR spectrum, inequivalency of the P–Me groups of the tridentate ligand is evidenced by the observation of four independent doublets in the range $\delta$ 0.9–1.4, whereas the molecule of PMe$_3$ gives a doublet centred at $\delta$ 1.33 ($J_{\text{P-H}}$ = 8.7 Hz). As already indicated, resonances attributable to an AMX spin system are discerned in the $^{31}$P{$^1$H} NMR spectrum. Those due to the $^{31}$P termini of the NP$_2$ ligand (A and X) show the effect of a strong $J$(P$_A$-P$_X$) coupling of 178 Hz, indicative of a mutual *trans* geometry. The single PMe$_3$ group (P$_M$), *cis* with respect to P$_A$ and P$_X$, appears as a triplet due to accidentally degenerate P$_A$-P$_M$ and P$_A$-P$_X$ couplings of 12 Hz. The room temperature $^{13}$C{$^1$H} NMR spectrum of **1*** consists of two broad, partially unresolved signals centred at about $\delta$ 213.5 and 217, suggestive of fluxionality. Accordingly, upon cooling to −80 °C, two well-resolved signals, each consisting of a doublet of doublets of doublets, are observed (see Experimental). The fluxionality of related *trans*-Mo(CO$_2$)$_2$ adducts has been studied in detail and demonstrated to consist of a synchronous motion of the two CO$_2$ ligands in which both molecules rotate in the same direction.[5b]

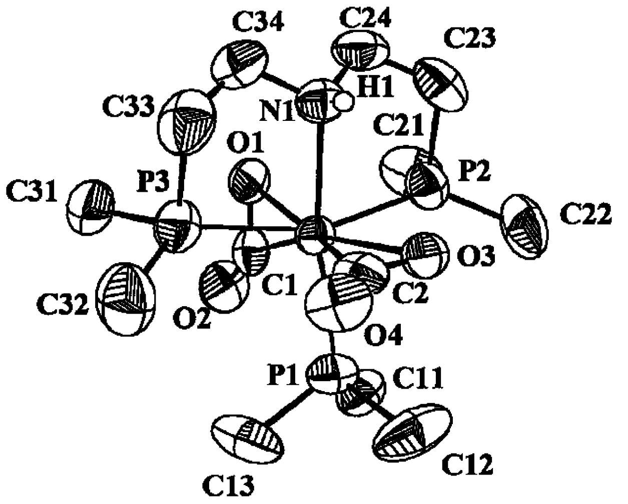


**Fig. 1** ORTEP view of the molecule in compound **1**.

The spectroscopic data discussed in the preceding paragraph supports the geometry proposed for complex **1** in eqn. (2). Unequivocal confirmation has been provided by single-crystal X-ray studies, whose results are presented in Fig. 1 and Tables 1 and 2. Compound **1** has a distorted octahedral geometry, with the CO$_2$ ligands side-on bonded to molybdenum through one of the C=O bonds. In agreement with theory,[10] and with structures of analogous derivatives,[5a] the two CO$_2$ ligands are mutually staggered, each one eclipsing a corresponding *trans*-L–Mo–L′ vector in the plane perpendicular to the CO$_2$–Mo–CO$_2$ axis. Bonding parameters within the Mo–CO$_2$ units are similar to those found for *trans*-Mo(CO$_2$)$_2$(PMe$_3$)$_3$(CN–*i*-Pr) and reveal, likewise, strong Mo–CO$_2$ bonding interactions. The Mo–C bond lengths in **1** (2.08 Å ave) are identical within experimental error to those in the above CN–*i*-Pr derivative and approach normal Mo–CO distances {1.970(4) and 2.03(1) Å, average values for the two types of CO groups in

**Table 1** Crystal data and structure refinement for compounds **1** and **4**

| | 1 | 4 |
|---|---|---|
| Empirical formula | C$_{13}$H$_{30}$MoNO$_4$P$_3$ (C$_3$H$_8$ )$_{0.5}$ | C$_{21}$H$_{56}$MoO$_{10}$P$_6$ · H$_2$O |
| Formula weight | 474.25 | 960.3 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | *C*2/*c* | *P*2$_1$/*n* |
| *a*/Å | 19.947(5) | 9.769(1) |
| *b*/Å | 11.670(2) | 16.333(1) |
| *c*/Å | 20.004(7) | 24.682(1) |
| *β*/° | 101.89(2) | 98.99(1) |
| *U*/Å$^3$ | 4557 (2) | 3889.9(5) |
| *Z* | 8 | 4 |
| *T*/K | 295 | 294 |
| *μ*/mm$^{-1}$ | 0.801 | 1.244 |
| Reflexions measured | 5616 | 11 422 |
| Unique reflexions | 5459 | 11 177 |
| *R*$_1$ (all data) | 0.236 | 0.0760 |
| *wR*$_2$ (all data) | 0.238 | 0.1038 |
| *R*$_1$ [*I* > 2*σ*(*I*)] | 0.064 | 0.0327 |
| *wR*$_2$ [*I* > 2*σ*(*I*)] | 0.173 | 0.0889 |

**Table 2** Main bond distances (Å) and angles (°) for compound **1**[a]

| | | | |
|---|---|---|---|
| Mo–Pl | 2.434(3) | C24–N1 | 1.45(2) |
| Mo–P2 | 2.481(3) | C34–N1 | 1.46(2) |
| Mo–P3 | 2.443(3) | C1–O1 | 1.284(11) |
| Mo–N1 | 2.270(7) | Cl–O2 | 1.199(10) |
| Mo–C1 | 2.088(9) | C2–O3 | 1.245(11) |
| Mo–O1 | 2.111(6) | C2–O4 | 1.234(11) |
| Mo–C2 | 2.085(9) | Hl–N1 | 0.91(11) |
| Mo–O3 | 2.138(6) | | |
| C1–Mo–C2 | 148.6(4) | C1–Mo–P2 | 92.7(3) |
| C1–Mo–O1 | 35.6(3) | C2–Mo–P2 | 113.0(3) |
| C2–Mo–O1 | 157.1(4) | O1–Mo–P2 | 84.1(2) |
| C1–Mo–O3 | 156.5(3) | O3–Mo–P2 | 78.9(2) |
| C2–Mo–O3 | 34.3(3) | N1–Mo–P2 | 79.5(2) |
| O1–Mo–O3 | 158.9(3) | P1–Mo–P2 | 97.8(1) |
| C1–Mo–N1 | 116.2(4) | P3–Mo–P2 | 156.0(1) |
| C2–Mo–N1 | 87.2(3) | C24–N1–C34 | 110.0(8) |
| O1–Mo–N1 | 80.7(3) | C24–N1–Mo | 113.7(6) |
| O3–Mo–N1 | 84.0(4) | C34–N1–Mo | 115.0(6) |
| C1–Mo–P1 | 76.2(3) | C24–N1–H1 | 105.8 |
| C2–Mo–P1 | 82.3(2) | C34–N1–H1 | 105.8 |
| O1–Mo–P1 | 111.6(2) | Mo–N1–H1 | 105.8 |
| O3–Mo–P1 | 83.2(2) | O2–C1–O1 | 131.2(9) |
| N1–Mo–P1 | 167.2(2) | O2–C1–Mo | 155.6(8) |
| C1–Mo–P3 | 84.9(3) | O1–C1–Mo | 73.2(5) |
| C2–Mo–P3 | 78.6(3) | C1–O1–Mo | 71.2(5) |
| O1–Mo–P3 | 80.2(2) | O4–C2–O3 | 131.6(10) |
| O3–Mo–P3 | 111.5(2) | O4–C2–Mo | 153.2(9) |
| N1–Mo–P3 | 80.1(2) | O3–C2–Mo | 75.2(5) |
| P1–Mo–P3 | 104.8(1) | C2–O3–Mo | 70.5(5) |

[a] Esd are given in parentheses

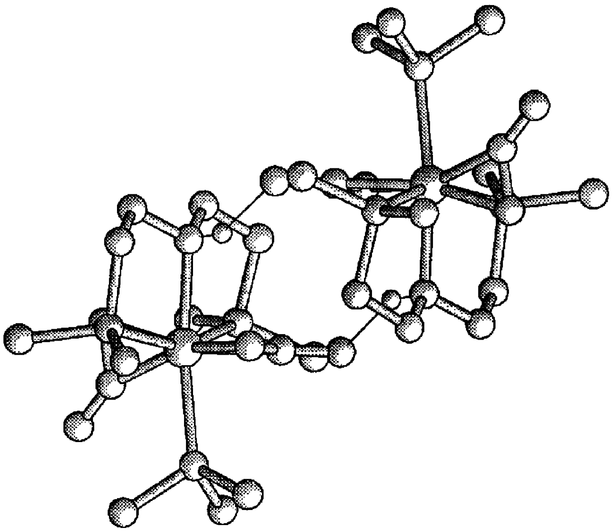


**Fig. 2** Molecular view of two molecules of **1** showing the hydrogen bonds.

*cis*-[Mo(CO)$_4$(PMe$_3$)$_2$][14]}. The same argument applies to the Mo–O bonds in **1** (2.12 Å ave). The two C–O bonds of each molecule of CO$_2$ appear to be of identical length within experimental error (Table 2) but are longer than in free CO$_2$ (1.16 Å).

The rigidity of the Mo(NP$_2$) chelate causes significant deviations of the corresponding bond angles from the ideal 90° and 180° values expected for an octahedral geometry. For instance, the two N–Mo–P angles approach 80°, whereas that between the two, supposedly *trans*, Mo–P bonds amounts to only 155.9(1)°. Considering this, the *mer* arrangement of the NP$_2$ ligand, although not unprecedented,[13] may seem unexpected. It appears that the flexibility of the N–CH$_2$–CH$_2$–P arms allow the tetrahedral nitrogen donor to be accommodated in a *mer* structure [angles centred on N: C24–N–Mo, 113.7(6)°; C34–N–Mo, 115.0(6)°; C24–N–C34, 110.0(8)°], in this way keeping the *trans*-Mo(CO$_2$)$_2$ moiety unaltered. The Mo–N and Mo–P separations have normal values (Table 2). An additional interesting feature of the solid state structure of **1** is the intermolecular hydrogen bond interaction that involves the aminic *H*NP$_2$ hydrogen and an *exo* (*i.e.*, non-coordinated) oxygen atom of a neighbouring molecule (Fig. 2). The observed H1–O$_{exo}$ distance of 2.2 Å (ave) is shorter that the sum of the van der Waals' radii[15] [1.40 (O) + 1.2 (H) = 2.60 Å], clearly in support of this proposal. Protic solvents like methanol (*vide supra*) may also participate in hydrogen bonding. An extended 3D network of hydrogen bonds has been shown to exist in the solid state structure of the η$^1$-CO$_2$ adduct [Ru(CO$_2$)(CO)(bipy)$_2$] · 3H$_2$O.[3b]

### Carbonyl carbonate complexes of Mo. Molecular structure of [Mo$_3$(μ$_2$-CO$_3$)(μ$_2$-O)$_2$(O)$_2$(CO)$_2$(H$_2$O)(PMe$_3$)$_6$] · H$_2$O (4).

In coordinating solvents, *cis*-[Mo(N$_2$)$_2$(PMe$_3$)$_4$] induces the reductive disproportionation of CO$_2$ with formation of the carbonyl carbonates [Mo(CO$_3$)(CO)(PMe$_3$)$_4$] and [Mo(CO$_3$)(CO)(PMe$_3$)$_3$]$_2$. Both complexes interconvert readily by loss or addition of PMe$_3$, and react with chelating diphosphine ligands (P-P) to afford the substitution products [Mo(CO$_3$)(CO)(P-P)(PMe$_3$)$_2$] and [Mo(CO$_3$)(CO)(P-P)$_2$].[8b]

In a like manner, addition of NP$_2$ to solutions of either of the above carbonato compounds allows the isolation of a yellow microcrystalline species [eqn. (3)] of composition [Mo(CO$_3$)(CO)(NP$_2$)(PMe$_3$)] (**2**):

$$[\mathrm{Mo(CO_3)(CO)(PMe_3)_4}] + \mathrm{NP_2} \xrightarrow{20\ ^\circ\mathrm{C}} \underset{\mathbf{2}}{[\mathrm{Mo(CO_3)(CO)(NP_2)(PMe_3)}]} + 3\ \mathrm{PMe_3} \qquad (3)$$

The presence of the NP$_2$ ligand in the molecules of **2** is indicated by the observation of an IR ν(N–H) band at 3300 cm$^{-1}$ and by its characteristic NMR parameters, detailed in the Experimental. On account of the appearance of an AX$_2$ spin system for the $^{31}$P nuclei of **2** ($\delta_A$ = 24.4, $\delta_X$ = 69.1; $^2J_{AX}$ = 19 Hz), the NP$_2$ ligand is suggested to adopt a *mer* conformation, as demonstrated by X-ray studies for **1**. A distinctive IR absorption at 1600 cm$^{-1}$ can be taken as diagnostic of bidentate, κ$^2$-*O*,*O′* coordination of the carbonate group.[16] This is not shifted in comparison with the starting material, whilst ν(CO) for the Mo–CO unit moves from 1810 cm$^{-1}$ in [Mo(CO$_3$)(CO)(PMe$_3$)$_4$] to 1780 cm$^{-1}$. It thus appears that replacement of three PMe$_3$ groups by NP$_2$ increases back-donation from Mo to CO. On the basis of the above data compound **2** can be considered structurally comparable to the parent carbonate [Mo(CO$_3$)(CO)(PMe$_3$)$_4$].[8b]

At variance with this result, only one PMe$_3$ ligand is substituted by CO when [Mo(CO$_3$)(CO)(PMe$_3$)$_4$] is reacted at room temperature, with 4 atm of carbon monoxide [eqn. (4)]:

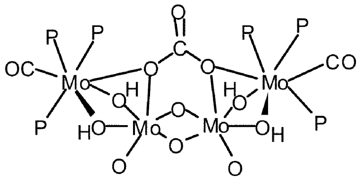
$$[\mathrm{Mo(CO_3)(CO)(PMe_3)_4}] + \mathrm{CO} \xrightarrow{20\ ^\circ\mathrm{C}} \underset{\mathbf{3}}{[\mathrm{Mo(CO_3)(CO)_2(PMe_3)_3}]} + \mathrm{PMe_3} \qquad (4)$$

The $^{31}$P{$^1$H} NMR spectrum of **3** recorded at 20 °C displays two broad resonances that convert into well-resolved triplet and doublet upon cooling to −80 °C [AX$_2$ spin system, $\delta_A$ −8.7, $\delta_X$ 35.1; $J$(P$_A$-P$_X$) = 11.7 Hz]. The well-defined band in the vicinity of 1600 cm$^{-1}$ due to the ν(C=O) of the carbonate shifts slightly to lower energy (1580 $cm^{-1}$), while the two CO groups are at the origin of absorptions at 1920 and 1820 $cm^{-1}$.

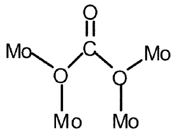
Somewhat unexpectedly, reduction to Mo(0) occurs upon mild heating (60 °C) of solutions of carbonato **3**. The reaction becomes cleaner when performed in the presence of CO; a mixture of the known carbonyl derivatives $[Mo(CO)_n(PMe_3)_{6-n}]$ ($n$ = 2, 3)[17] is obtained under these conditions. Analysis of the volatiles reveal the presence of $CO_2$ further identified by its known, characteristic reaction[9a,b] with the complex $[\overline{Ni(CH_2CMe_2\text{-}o\text{-}C}_6H_4)(PMe_3)_2]$, in the presence of small amounts of water, to give the carbonate $[Ni_2(CH_2CMe_2Ph)_2(\mu\text{-}CO_3)(PMe_3)_3]$. These observations indicate that, upon heating, the $CO_3^{2-}$ and CO ligands of **3** undergo an oxidative conproportionation to $CO_2$ [eqn. (5)], with concomitant reduction of the metal from Mo(II) to Mo(0):

$$CO_3^{2-} + CO - 2\,e^- \rightarrow 2\,CO_2 \qquad (5)$$

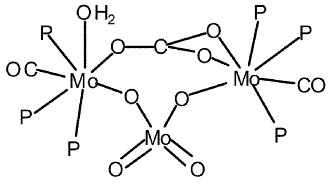
Besides $[Mo(CO_3)(CO)(PMe_3)_4]$ and $[Mo(CO_3)(CO)(PMe_3)_3]_2$, the reaction of *cis*-$[Mo(N_2)_2(PMe_3)_4]$ and $CO_2$ provides, under certain conditions, small amounts of another carbonato derivative, namely the known[8b] tetranuclear $[Mo_4(CO_3)(\mu\text{-}O)_2(\mu\text{-}OH)_4(CO)_2(PMe_3)_6]$. As depicted schematically in **D** and **E**, this compound contains a unique bridging carbonate group. Heating a THF solution of $[Mo(CO_3)(CO)(PMe_3)_3]_2$ plus added water, at 50 °C, gives the same $Mo_4$ species, albeit once more in low yields (*ca.* 10%).



**D**



**E**



**4**

In an attempt to find a reliable, higher-yield synthetic procedure, $[Mo(CO_3)(CO)(PMe_3)_4]$ and $[Mo(CO_3)(CO)(PMe_3)_3]_2$ have been reacted with $H_2O$ under different experimental conditions, including in the presence of air. Acetone, methanol and tetrahydrofuran, as well as some of their mixtures, have been tested with controlled addition of $H_2O$ at room temperature and at 50–60 °C. A sufficiently better route to the $Mo_4$ complex has not been found but nevertheless a somewhat related $Mo_3$ complex of composition $[Mo_3(\mu_2\text{-}CO_3)(\mu_2\text{-}O)_2(O)_2(CO)_2(H_2O)(PMe_3)_6]\cdot H_2O$ (**4**) has been isolated. Due to its insolubility in common organic solvents, reliable NMR data have not been recorded. Its IR spectrum shows a band at *ca.* 3500 $cm^{-1}$ due to a coordinated molecule of water, along with carbonyl absorptions at 1770 and 1755 $cm^{-1}$ and others attributable to the carbonate (1515 and 1280 $cm^{-1}$) and $PMe_3$ (945 $cm^{-1}$) ligands. The structure of the molecule of **4** has been unambiguously determined by a single-crystal X-ray study, whose results are presented in Fig. 3 and Tables 1 and 3.

As can be seen, complex **4** is a mixed-valence Mo(II)–Mo(VI) trinuclear species that consists of two seven-coordinate Mo(II) atoms bridged by a $\kappa^2\text{-}O,O'\text{-}MoO_4^{2-}$ unit. The structural relation of the moiety comprised by the two Mo(II) atoms with $[Mo(CO_3)(CO)(PMe_3)_3]_2$ and the structurally characterized $PMe_2Ph$ analogue is evident.[7a] One of the $\mu\text{-}CO_3^{2-}$ ligands of $[Mo(CO_3)(CO)(PMe_3)_3]_2$ is lost, being formally replaced by the molybdate group. As the remaining $CO_3^{2-}$ acts as a $\kappa^2\text{-}O,O'$ toward Mo(2) and as $\kappa^1\text{-}O''$ toward Mo(1), the coordination of the latter is completed by a molecule of $H_2O$. Note that the "$Mo(CO)(PMe_3)_3$" terminal fragments are maintained both in **4** and in the $Mo_4$ complex referred to above. In complex **4**, the $CO_3^{2-}$ group that bridges these fragments is planar: the three O–C–O angles have similar values that add together to practically 360°. The three C–O bonds do not differ appreciably in length and the same can be said for the three $Mo\text{–}OCO_2$ separations.

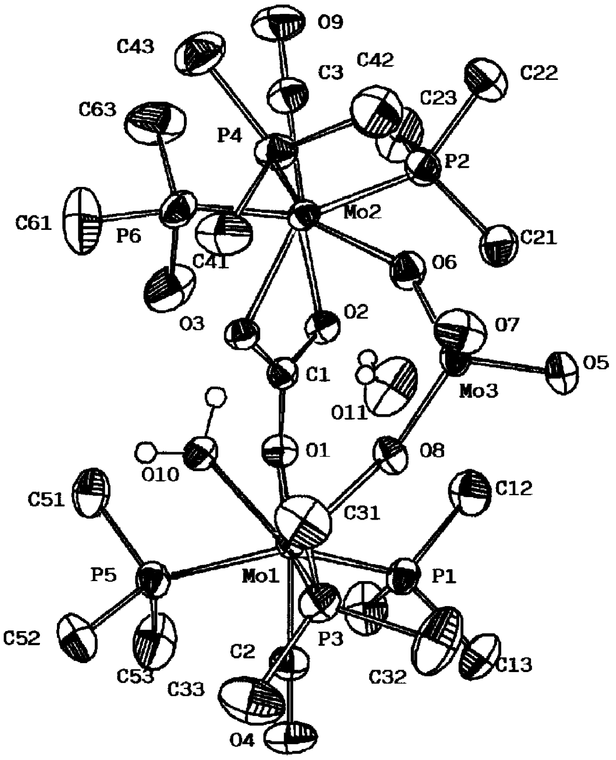


**Fig. 3** ORTEP view of the molecule of compound **4**.

Despite its bidentate nature, the bridging $MoO_4^{2-}$ group has a nearly tetrahedral geometry, with O6–Mo3–O7 [108.0(1)°] and O5–Mo3–O8 [111.1(1)°] showing the largest deviations with respect to the 109.5° ideal value. The two $Mo\text{–}O_t$ bonds (Mo3–O5 and Mo3–O7) are identical within experimental error and average 1.74 Å. The bridging Mo–O bonds are also of equal length (1.77 Å, average value) and only slightly longer than the $Mo\text{–}O_t$. For comparative purposes, the Mo–O distance in $K_2MoO_4$ is 1.76(1) Å.[18] Trimetallic units are bonded among themselves, *via* intermolecular hydrogen bonds (Table 4) through the coordinated water molecules in the [010] direction and through the uncoordinated ones in the [100] direction. This arrangement gives rise to infinite layers perpendicular to the [001] direction of composition $\{[Mo_3(CO)_2(PMe_3)_6(H_2O)(\mu_2\text{-}CO_3)(O)_2(\mu_2\text{-}O_2)]H_2O\}^{\infty}$. The only two oxygen atoms that are not involved in the connectivity inside these layers, those of the carbonyl groups O(4) and O(9), are pointing outside, toward the interlayer space (Fig. 4).

The identification of the molybdate group in the structure of **4** allows the design of a rational preparative route, consisting in the reaction of stoichiometric amounts of $[Mo(CO_3)(CO)(PMe_3)_3]_2$, dissolved in THF, and of $Na_2MoO_4$, dissolved in water (yields are about 50%). Even though **4** may be an intermediate along the path leading to the $Mo_4$ compound, we have been unable to find consistent proof for this hypoth-

**Table 3** Main bond distances (Å) and angles (°) for compound **4**[a]

| | | | |
|---|---|---|---|
| Mo1–Pl | 2.437(1) | Mo2–O6 | 2.189(2) |
| Mo1–P3 | 2.438(1) | Mo2–C1 | 2.598(3) |
| Mo1–P5 | 2.452(1) | Mo2–C3 | 1.918(4) |
| Mo1–O1 | 2.232(2) | Mo3–O5 | 1.749(3) |
| Mo1–O8 | 2.167(2) | Mo3–O6 | 1.773(2) |
| Mo1–O10 | 2.271(2) | Mo3–O7 | 1.739(3) |
| Mo1–C2 | 1.887(4) | Mo3–O8 | 1.783(2) |
| Mo2–P2 | 2.412(1) | O1–C1 | 1.265(4) |
| Mo2–P4 | 2.424(1) | O2–C1 | 1.284(4) |
| Mo2–P6 | 2.442(1) | O3–C1 | 1.304(4) |
| Mo2–O2 | 2.202(2) | O4–C2 | 1.188(4) |
| Mo2–O3 | 2.204(2) | O9–C3 | 1.181(4) |
| O10–Mo1–C2 | 130.1(1) | P6–Mo2–C3 | 76.7(1) |
| O8–Mo1–C2 | 131.5(1) | P6–Mo2–O6 | 158.75(7) |
| O8–Mo1–O10 | 81.98(9) | P6–Mo2–O3 | 79.45(6) |
| O1–Mo1–C2 | 127.3(1) | P6–Mo2–O2 | 82.53(6) |
| O1–Mo1–O10 | 86.35(8) | P4–Mo2–C3 | 75.2(1) |
| O1–Mo1–O8 | 82.81(8) | P4–Mo2–O6 | 76.50(7) |
| P5–Mo1–C2 | 73.6(1) | P4–Mo2–O3 | 90.10(6) |
| P5–Mo1–O10 | 79.43(7) | P4–Mo2–O2 | 145.35(6) |
| P5–Mo1–O8 | 154.94(7) | P4–Mo2–P6 | 109.66(4) |
| P5–Mo1–O1 | 79.4(6) | P2–Mo2–C3 | 73.0(1) |
| P3–Mo1–C2 | 74.5(1) | P2–Mo2–O6 | 79.27(6) |
| P3–Mo1–O10 | 79.99(6) | P2–Mo2–O3 | 140.30(6) |
| P3–Mo1–O8 | 78.04(6) | P2–Mo2–O2 | 84.13(6) |
| P3–Mo1–O1 | 157.81(6) | P2–Mo2–P6 | 113.30(4) |
| P3–Mo1–P5 | 114.70(3) | P2–Mo2–P4 | 117.31(3) |
| P1–Mo1–C2 | 74.3(1) | O7–Mo3–O8 | 109.5(1) |
| P1–Mo1–O10 | 155.59(7) | O6–Mo3–O8 | 110.9(1) |
| P1–Mo1–O8 | 79.98(6) | O6–Mo3–O7 | 108.0(1) |
| P1–Mo1–Ol | 75.22(6) | O5–Mo3–O8 | 111.1(1) |
| P1–Mo1–P5 | 111.92(3) | O5–Mo3–O7 | 108.9(1) |
| P1–Mo1–P3 | 111.89(3) | O5–Mo3–O6 | 108.3(1) |
| O6–Mo2–C3 | 124.4(1) | O2–C1–O3 | 115.3(3) |
| O3–Mo2–C3 | 145.5(1) | O1–C1–O3 | 122.1(3) |
| O3–Mo2–O6 | 80.24(8) | O1–C1–O2 | 122.7(3) |
| O2–Mo2–C3 | 139.4(1) | Mo1–C2–O4 | 179.2(3) |
| O2–Mo2–O6 | 81.84(9) | Mo2–C3–O9 | 179.1(3) |
| O2–Mo2–O3 | 59.49(8) | | |

[a] Esd are given in parentheses

esis. An alternative possibility is that they form independently. Regardless of this, their insolubility in common solvents permits their isolation and ulterior characterization.

**Table 4** Hydrogen bond distances (Å) and angles (°) for **4**

| O–H···O[a] | d(O–H) | d(H···O) | d(O···O) | ∠(O–H···O) |
|---|---|---|---|---|
| O10–H101···O5′ | 0.77(6) | 1.94(6) | 2.683(4) | 164(5) |
| O10–H102···O3 | 0.96(6) | 1.74(6) | 2.599(4) | 148(5) |
| O11–H111···O7″ | 0.92(6) | 1.99(7) | 2.902(6) | 172(5) |
| O11–H112···O2 | 0.94(6) | 1.98(6) | 2.890(5) | 160(5) |

[a] Esd are given in parentheses. Symmetry code: (′) 3/2 − *x*, *y* − 1/2, 1/2 − *z*. (″) *x* − 1, *y*, *z*.

## Conclusion

In summary, the electronically favourable *trans*-$Mo(CO_2)_2$ conformation, with staggered $CO_2$ ligands, characteristic of the complex *trans*-$[Mo(CO_2)_2(PMe_3)_4]$ is retained during the substitution of three molecules of $PMe_3$ by the tridentate $HN(CH_2CH_2PMe_2)_2$ ligand ($NP_2$), to give compound **1**. The isomeric carbonyl carbonate complex, $[Mo(CO_3)(CO)(NP_2)(PMe_3)]$, has also been prepared, along with an unusual trinuclear complex **4**, shown by X-ray studies to consist of two seven-coordinate Mo(II) atoms bridged by a bidentate $MoO_4^{2-}$ unit. The trimetallic units of **4** are bonded among themselves by means of intermolecular hydrogen bonds that involve both the coordinated and the uncoordinated water molecules of **4**, forming the infinite layers schematically represented in Fig. 4.

During the revision of this work, a linear, *O*-coordinated carbon dioxide complex of uranium has been reported.[19]

## Experimental

All preparations and manipulations were performed under an oxygen-free nitrogen atmosphere using conventional Schlenk techniques. Solvents were rigorously dried and degassed before use. The complexes *trans*-$[Mo(CO_2)_2(PMe_3)_4]$,[5] $[Mo(CO_3)(CO)(PMe_3)_4]$,[8] $[Mo(CO_3)(CO)(PMe_3)_3]_2$,[8] and $[\overline{Ni(CH_2C(Me)_2\text{-}o\text{-}C}_6H_4)(PMe_3)_2]$[9] and the phosphine $HN(CH_2CH_2PMe_2)_2$[12] were prepared according to literature methods. NMR spectra were acquired with Varian XL-200 and Bruker DRX 500 MHz spectrometers. Microanalyses were carried out by the Microanalytical Service of the University of Seville. Despite all our attempts, satisfactory analytical data have been obtained only for **1** and **4**.

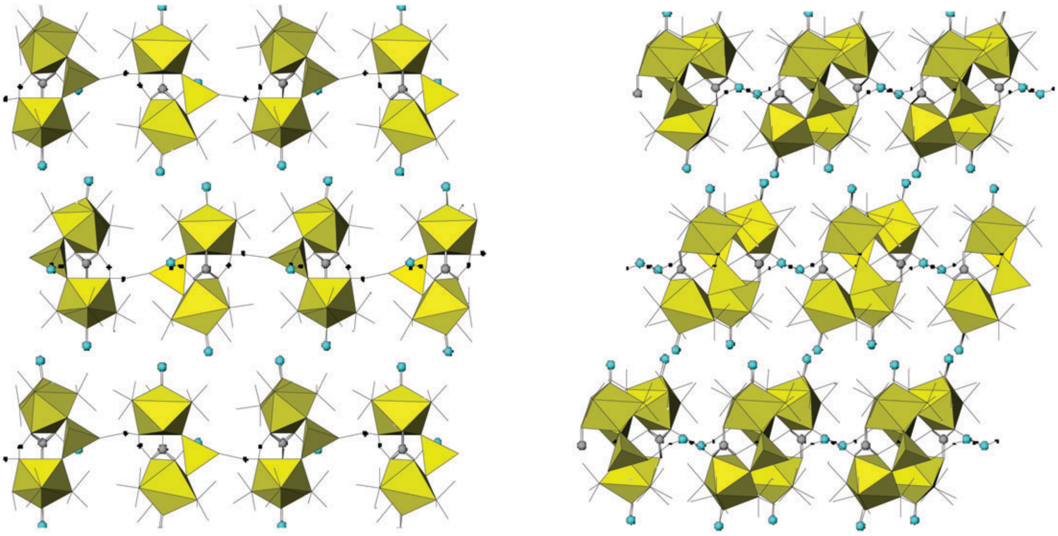
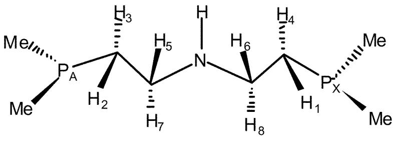


**Fig. 4** View of the packing showing the connections among the Mo trimetallic units of **4** through the coordinated and uncoordinated water molecules in the *b* (left) and *a* (right) directions, respectively. Blue circles are terminal oxygen atoms (O4 and O9) and uncoordinated water oxygen (O11), grey circles represent the carbon atoms of the carbonate (C1).

## Syntheses

**_trans_-$[Mo(CO_2)_2(HN(CH_2CH_2PMe_2)_2)(PMe_3)]$ (1).** A solution of *trans*-$[Mo(CO_2)_2(PMe_3)_4]$ (0.1 g, 0.2 mmol) in tetrahydrofuran (30 ml) was treated with a slight excess of $HN(CH_2CH_2PMe_2)_2$ (0.048 g, 0.25 mmol). After 2 h of stirring, the volatiles were removed under reduced pressure. The residue was extracted with a 1 : 1 mixture of $Et_2O$–petroleum ether, and the resulting solution was cooled to −20 °C, giving yellow crystals of complex **1**. Yield: 70%. Anal. found: C, 34.0; H, 6.5; N, 3.1; calcd. for $C_{13}H_{30}MoNO_4P_3$: C, 34.5; H, 6.7; N, 3.1%. IR ($cm^{-1}$): 3500, 3200, $\nu$(N–H); 1660, 1150, 1100, $\nu$(C=O); 950, $\nu$(P–C). NMR (see **F** for numbering scheme): $^1H$ ($CD_3OD$, 500 MHz) $\delta$ 3.96 [br t, N–H, $J(HH_6)$ = 11.6, $J(HH_5)$ = 11.6, $J(HH_7)$ = 3.5, $J(HH_8)$ = 3.5, $J(HP_X)$ = 37.2 Hz ], 3.19 [m, $H_8$, $J(H_8H_6)$ = 11.6, $J(H_8\text{-}H_1)$ = 4.8, $J(H_8\text{-}H_7)$ = 2.1, $J(H_8\text{-}H_4)$ = 1.2 Hz], 3.14 [m, $H_7$, $J(H_7\text{-}H_5)$ = 11.6, $J(H_7\text{-}H_2)$ = 4.8, $J(H_7\text{-}H_3)$ = 2.1, $J(H_7\text{-}P_A)$ = 35.8 Hz], 2.58 [m, $H_6$, $J(H_6\text{-}H_1)$ = 14.7, $J(H_6\text{-}H_4)$ = 3.2, $J(H_6\text{-}P_X)$ = 7.8 Hz ], 2.50 [m, $H_5$, $J(H_5\text{-}H_1)$ = 14.8, $J(H_5\text{-}H_3)$ = 3.2, $J(H_5\text{-}P_A)$ = 37.2 Hz], 2.13 [br t, $H_4$, $J(H_4\text{-}H_1)$ = 14.4, $J(H_4\text{-}P_X)$ = 13.2 Hz], 1.99 [br t, $H_3$, $J(H_3\text{-}H_2)$ = 12.9, $J(H\text{-}P_A)$ = 12.9 Hz], 1.86 [m, $H_2$, $J(H_2\text{-}P_A)$ = 4.1 Hz], 1.78 [d, 3H, $P_A$–Me, $J$(H-P) = 9.1 Hz], 1.66 [m, $H_1$, $J(H_1\text{-}P_X)$ = 4.3 Hz], 1.39 [d, 3H, $P_X$–Me, $J$(H-P) = 7.8 Hz], ], 1.33 [d, 9H, P–$Me_3$, $J$(H-P) = 8.7 Hz], ], 1.30 [d, 3H, $P_X$–Me, $J$(H-P) = 8.3 Hz], 0.94 [d, 3H, $P_A$–Me, $J$(H-P) = 8.1 Hz]; $^{13}C\{^1H\}$ (75 MHz, $CH_3OH$–$CD_3COCD_3$, −80 °C, sample 30% enriched in $^{13}CO_2$) $\delta$ 218.6 [ddd, 1 $CO_2$, $J$(C-P) = 49.1, $J$(C-P) = 15.5, $J$(C-P) = 7.8 Hz], 214.1 [ddd, 1 $CO_2$, $J$(C-P) = 43.7, $J$(C-P) = 18.5, $J$(C-P) = 10.5 Hz]. At 25 °C, these resonances appear as two multiplets with the same chemical shifts. $^{13}C\{^1H\}$ (125 MHz, $C_6D_6$, 25 °C, non-enriched sample) $\delta$ 210.5 [m, 1 $CO_2$], 208.0 [m, 1 $CO_2$], 49.3 [s, $CH_2$], 48.0 [s, $CH_2$], 34.1 [d, P–$CH_2$, $J$(C-P) = 35 Hz ], 31.8 [d, P–$CH_2$, $J$(C-P) = 28 Hz ], 20.0 [d, $P(CH_3)_3$, $J$(C–P) = 40 Hz ], 12.2 [d, $P_A$–Me, $J$(C-P) = 39 Hz], 9.5 [d, $P_X$–Me, $J$(C-P) = 28.5 Hz], 9.0 [d, $P_X$–Me, $J$(C-P) = 28.1 Hz], 8.7 [d, $P_A$–Me, $J$(C-P) = 29.1 Hz]; $^{31}P\{^1H\}$ ($C_6D_6$, 121 MHz), AMX spin system, $\delta_A$ 28.3 [$P_A$, $J(P_A\text{-}P_M)$ = 12, $J(P_A\text{-}P_X)$ = 178 Hz], $\delta_M$ 22.9 [$PMe_3$, $J(P_M\text{-}P_X)$ = 12 Hz], $\delta_X$ 15.0 [$P_X$].



**F**

**$[Mo(CO_3)(CO)(HN(CH_2CH_2PMe_2)_2)(PMe_3)]$ (2).** To a stirred solution of $[Mo(CO_3)(CO)(PMe_3)_4]$ (0.1 g, 0.2 mmol), an equimolar amount of $HN(CH_2CH_2PMe_2)_2$ was added (0.024 g, 0.125 mmol). The addition induced an immediate change in colour from the initial red to orange, whereupon the mixture was stirred for 1 h and the volatiles were then removed. The residue was washed with $Et_2O$ (2 × 20 ml) to give complex **2** as a yellow microcrystalline material in 60% yield. IR ($cm^{-1}$): 3300, $\nu$(N–H); 1750, $\nu$(CO); 1600, 1250, $\nu(CO_3)$; 950, $\nu$(P–C). $^{31}P\{^1H\}$ (THF–$CD_3COCD_3$, 81 MHz), $AX_2$ spin system, $\delta_A$ 24.5, $\delta_X$ 69.1 [$J(P_A\text{-}P_X)$ = 19 Hz]; $^1H$ ($CD_3OD$, 200 MHz) 1.65 [d, 6H, 2 Me, $J$(H-P) = 10.2 Hz], 1.45 [d, 6H, 2 Me, $J$(H-P) = 9.8 Hz], 1.37 [d, 9H, $PMe_3$, $J$(H-P) = 8.6 Hz], the methylene signals appeared as broad multiplets centred at 4.55, 3.22, 2.64 and 2.00 ppm (2 H each).

**$[Mo(CO_3)(CO)_2(PMe_3)_3]$ (3).** A solution of $[Mo(CO_3)(CO)(PMe_3)_4]$ (0.1 g, 0.2 mmol) in methanol (3 ml) was pressurised with CO (4 atm) and the mixture was stirred for 2 h at room temperature. The initially red solution turned to orange; the solvent was then removed under vacuum and the residue washed with $Et_2O$ (2 × 20 ml). Yellow microcrystalline material of complex **3** was obtained in 65% yield. Selected spectroscopic data: IR ($cm^{-1}$) 1920, 1820, $\nu$(CO); 1580, $\nu(CO_3)$; 955, $\nu$(P–C). $^{31}P\{^1H\}$ (THF–$CD_3COCD_3$, 81 MHz) 32.5 (br s, 2 P), −10.5 (br s, 1 P). These resonances resolved into an $AX_2$ spin system when recording the spectrum at −80 °C: $\delta_A$ −8.7, $\delta_X$ 35.1 [$J(P_A\text{-}P_X)$ = 11.7 Hz]. The proton and carbon spectra gave broad signals with no useful information being gained from them.

Heating a methanolic solution of complex **3** at 60 °C under CO (1 atm) for 3 h results in a change of colour from the initial orange to dark yellow. The reaction gases are trapped inside of a liquid nitrogen-cooled ampoule, a white solid ($CO_2$) being obtained. The former solution was investigated by NMR, a mixture of carbonyls of composition $[Mo(CO)_6(PMe_3)_{6-n}]$ being detected. The trapped gas was transferred into a flask containing a wet solution of the nickelacycle compound and the mixture stirred for 2 h, before volatile removal and NMR investigation of the crude sample.

**$[Mo_3(CO)_2(PMe_3)_6(H_2O)(\mu_2\text{-}CO_3)(O)_2(\mu_2\text{-}O)_2]$ (4).** $[Mo(CO_3)(CO)(PMe_3)_4]$ (0.2 g, 0.4 mmol) was suspended in acetone (8 ml) and water was added dropwise until dissolution was achieved. The red-orange solution was left undisturbed for a week. Crystals (25% yield) were then collected by filtration, the material being too insoluble to perform NMR studies. Some of the crystals were suitable for an X-ray diffraction study (see below) that led to the characterization as the title compound. Anal. found: C, 26.0; H, 5.6; calcd. for $C_{21}H_{56}Mo_3O_{10}P_6 \cdot H_2O$: C, 26.2; H, 6.0%. IR ($cm^{-1}$) 1770, 1755, $\nu$(CO); 1515, 1280, $\nu(CO_3)$; 945, $\nu$(P–C).

An alternative procedure has been developed. A solution of $Na_2MoO_4$ in water (5 ml) was transferred into a flask containing $[Mo(CO_3)(CO)(PMe_3)_4]$ (0.2 g, 0.4 mmol) suspended in acetone (10 ml). Upon addition, the starting material dissolved at the same time that a new orange-coloured solid came out of the solution. The mixture was stirred overnight, the solid filtered off, washed with THF and $Et_2O$, and dried under vacuum. The resulting orange solid displayed an IR spectrum identical to that described above. Yield: 50%.

## Crystal structure determinations for compounds 1 and 4†

A summary of the fundamental crystal data is given in Table 1. In both cases, a crystal of prismatic shape was coated with resin epoxy and mounted in a Kappa diffractometer. Data were collected using graphite monochromated Mo-K$\alpha$ ($\lambda$ = 0.71069 Å) radiation. The cell dimensions were refined by least-squares fitting of the $\theta$ values of 25 reflections. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Mo and P were taken from the International Tables for X-ray Crystallography.[20] The structure was solved by Patterson and Fourier methods. An empirical absorption correction was applied at the end of the isotropic refinement. A final refinement was undertaken with anisotropic thermal parameters for the non-hydrogen atoms. In the case of complex **1**, the H1 atom was located in a difference synthesis and its coordinates were refined. Final difference synthesis showed three peaks that were assigned to 3-carbon chains originating from the petroleum ether used as the solvent. Most of the calculations were carried out with the SHELXTL system.[21]

---

† CCDC reference numbers 231960 (**1**) and 231961 (**4**). See http://www.rsc.org/suppdata/nj/b4/b409385b/ for crystallographic data in .cif or other electronic format.

## Acknowledgements

We thank the Junta de Andalucía for financial support (Acciones Coordinadas).

## References

1 T. G. Spiro and W. M. Stigliani, in *Chemistry of the Environment*, Prentice Hall, Upper Saddle River, New Jersey, 1996, ch. 2.

2 (*a*) S. L. Wells and J. DeSimone, *Angew. Chem., Int. Ed.*, 2001, **40**, 518; (*b*) X. Yin and J. R. Moss, *Coord. Chem. Rev.*, 1999, **181**, 27; (*c*) D. H. Gibson, *Chem. Rev.*, 1996, **96**, 2063; (*d*) K. Tanaka, *Adv. Inorg. Chem.*, 1995, **43**, 409; (*e*) P. G. Jessop, T. Ikariya and R. Noyori, *Chem. Rev.*, 1995, **95**, 259; (*f*) W. Leitner, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2207.

3 (*a*) J. C. Calabrese, T. Herskovictz and J. B. Kinney, *J. Am. Chem. Soc.*, 1983, **105**, 5914; (*b*) H. Tanaka, H. Nagano, S. Peng and K. Tanaka, *Organometallics*, 1992, **11**, 1450.

4 For some examples of $\kappa^2$-*C*,*O*–M, see: (*a*) M. Aresta, C. F. Nobile, V. G. Albano, E. Forni and M. Manassero, *J. Chem. Soc., Chem. Commun.*, 1975, 36; (*b*) M. Aresta and C. F. Nobile, *J. Chem. Soc., Dalton Trans.*, 1977, 708; (*c*) G. S. Bristow, P. B. Hitchcock and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1981, 1145; (*d*) S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Gaustini, *J. Am. Chem. Soc.*, 1985, **107**, 2985.

5 (*a*) R. Alvarez, E. Carmona, J. M. Marín, M. L. Poveda, E. Gutiérrez-Puebla and A. Monge, *J. Am. Chem. Soc.*, 1986, **108**, 2286; (*b*) E. Carmona, A. K. Hughes, M. A. Muñoz, D. O'Hare, P. J. Pérez and M. L. Poveda, *J. Am. Chem. Soc.*, 1991, **113**, 9210.

6 (*a*) G. Fachinetti, C. Floriani, A. Chiesi-Villa and C. Gaustini, *J. Am. Chem. Soc.*, 1979, **101**, 1767; (*b*) J. C. Bryan, S. J. Geib, A. L. Rheingold and J. M. Mayer, *J. Am. Chem. Soc.*, 1987, **109**, 2826.

7 (*a*) J. Chatt, M. Kubotta, G. J. Leigh, T. C. March, R. Mason and D. J. Yarrow, *J. Chem. Soc., Chem. Commun.*, 1974, 1033; (*b*) S. Inoue and N. Yamazaki, *Organic and Bioinorganic Chemistry of Carbon Dioxide*, Halsted Press, Tokyo, Japan, 1982; (*c*) A. D. Palmer and R. Van Edik, *Chem. Rev.*, 1983, **83**, 651; (*d*) L. K. Fong, J. R. Fox and N. J. Cooper, *Organometallics*, 1987, **6**, 223.

8 (*a*) R. Alvarez, E. Carmona, A. Galindo, E. Gutiérrez, J. M. Marín, A. Monge, M. L. Poveda, C. Ruíz and J. M. Savariault, *Organometallics*, 1989, **8**, 2430; (*b*) R. Alvarez, J. L. Atwood, E. Carmona, P. J. Pérez, M. L. Poveda and R. D. Rogers, *Inorg. Chem.*, 1991, **30**, 1493.

9 (*a*) E. Carmona, P. Palma, M. Paneque, M. L. Poveda, E. Gutiérrez-Puebla and A. Monge, *J. Am. Chem. Soc.*, 1986, **108**, 6424; (*b*) E. Carmona, E. Gutiérrez-Puebla, J. M. Marín, A. Monge, M. Paneque, M. L. Poveda and C. Ruíz, *J. Am. Chem. Soc.*, 1989, **111**, 2883; (*c*) E. Carmona, J. M. Marín, P. Palma, M. Paneque and M. L. Poveda, *Inorg. Chem.*, 1989, **28**, 1895; (*d*) M. K. Reinking, J. Ni, P. E. Fanwick and C. P. Kubiak, *J. Am. Chem. Soc.*, 1989, **111**, 6454.

10 E. Sánchez-Marcos, R. Caballol, G. Trinquier and J.-C. Barthelat, *J. Chem. Soc., Dalton Trans.*, 1987, 2373.

11 T. Herskovitz and L. J. Guggenberger, *J. Am. Chem. Soc.*, 1976, **98**, 1615.

12 A. A. Danopoulos and P. G. Edwards, *Polyhedron*, 1989, **8**, 1767.

13 (*a*) A. R. Willis, P. G. Edwards, H. Harman and M. B. Hursthouse, *Polyhedron*, 1989, **9**, 1457; (*b*) A.-R. H. Al-Soudani, A. S. Batsanov, P. G. Edwards and J. A. K. Howard, *J. Chem. Soc., Dalton Trans.*, 1994, 987; (*c*) P. G. Edwards, P. W. Read, M. B. Hursthouse and K. M. Abdul Malik, *J. Chem. Soc., Dalton Trans.*, 1994, 971; (*d*) M. D. Fryzuk, T. S. Haddad and S. J. Rettig, *Organometallics*, 1991, **10**, 2026; (*e*) M. D. Fryzuk and C. D. Montmongery, *Coord. Chem. Rev.*, 1989, **95**, 1; (*f*) C. Bianchini, D. Masi, A. Romerosa, F. Zanobini and M. Peruzzini, *Organometallics*, 1999, **18**, 2376; (*g*) C. Bianchini, M. Peruzzini, F. Zanobini, C. Lopez, I. de los Ríos and A. Romerosa, *Chem. Commun.*, 1999, 443; (*h*) F. G. N. Cloke, P. B. Hitchcock and J. B. Love, *J. Chem. Soc., Dalton Trans.*, 1995, 25; (*i*) R. R. Schrock, A. L. Casado, J. T. Goodman, L.-Ch. Liang, P. J. Bonitatebus, Jr. and W. M. Davis, *Organometallics*, 2000, **19**, 5325.

14 F. A. Cotton, D. J. Darensbourg, S. Klein and B. W. S. Kolthammer, *Inorg. Chem.*, 1982, **21**, 2661.

15 L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, New York, 3rd edn., 1960.

16 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley and Sons, New York, 5th edn., 1997.

17 R. Mathieu, M. Lenzi and R. Poilblanc, *Inorg. Chem.*, 1970, **9**, 2030.

18 B. M. Gatehouse and P. Leverett, *J. Chem. Soc. A*, 1969, 848.

19 I. Castro-Rodríguez, H. Nakai, L. N. Zakharov, A. L. Rheingold and K. Meyer, *Science*, 2004, **305**, 1757.

20 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, UK, 1974, vol. **IV**, p. 72.

21 Software for the *SMART System*, V5.04, and *SHELXTL*, V5.1, Bruker–Siemens Analytica X-ray Instrument, Inc., Madison, WI, 1998.