Journal of Organometallic Chemistry, 410 (1991) 335–345
Elsevier Sequoia S.A., Lausanne
JOM 21788

Reactivity of carbon monoxide towards high valent molybdenum complexes

Richard Laï*, Sylvie Le Bot and Fatiha Djafri
E.N.S.S.P.I.C.A.M., URA 1410, Université Aix-Marseille III, 13013 Marseille (France)

(Received January 3rd, 1991)

Abstract

Reaction of carbon monoxide (3 atm) with $Mo(O)_2(mes)_2$ (mes = mesityl = $C_6H_2Me_3$-2,4,6) in pyridine at room temperature affords dimesityl ketone **1** (5%) and 1,1′-bis(mesitoyl)-1,1′,4,4′-tetrahydro-4,4′-bipyridine **2** (25%), the molecular structure of which has been determined by an X-ray diffraction study. The formation of **2** represents the first example of *N*-acylation of a pyridine by CO mediated by a transition metal complex. It has been shown that the relative ratio of **1** and **2** is dependent on the reaction conditions and that the presence of pyridine is essential for the formation of **1**. Reactions of CO with the isoelectronic complex $Mo(N^tBu)_2mes_2$ contrast sharply with $Mo(O)_2mes_2$ and, under the same conditions, no dihydropyridine is formed, the sole identified products being **1** (60%) and mesityltertiobutyl amide $HN(^tBu)COmes$ (40%). In light of the experimental results and of extended Hückel calculations on dioxo and diimido d^0 molybdenum complexes, a tentative mechanism for the formation of **2** is proposed which involves oxycarbene-like intermediates in the case of the more electrophilic dioxo molybdenum species.

Introduction

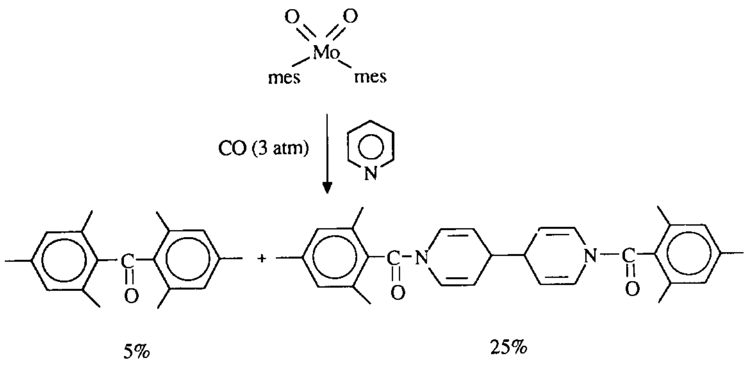
Except in the case of actinide, lanthanide, and oxophilic early transition elements, carbon monoxide coordination to a metal center and conventional transition-metal mediated carbonylation reactions usually involve moderate to low oxidation state complexes [1]. This situation can be reasonably understood in terms of the weak π-backbonding ability and low tendency to form stable carbonyl complexes of metal ions in formal high oxidation state. However, some recently reported results have shown that CO, olefin and acetylene coordination can be achieved with d^2 [2] or even d^0 species [3,4]. We have also reported *N*-acylation of pyridine by CO mediated by a molybdenum dioxo complex [5]. In order to throw light on this unusual reactivity of carbon monoxide, additional experiments were carried out and the influence of various factors in this reaction has been studied as well as the comparative carbonylation of the isoelectronic diimido complex $Mo(N^tBu)_2mes_2$. We report below the results of this study together with a discussion of the mechanism of these carbonylations reactions.

0022-328X/91/$03.50

Results and discussion

Formation of dihydropyridine dimers from Mo(O)$_2$mes$_2$, CO and pyridines. X-ray structure of 1,1′-bis(mesitoyl)-1,1′,4,4′-tetrahydro-4,4′-bipyridine

As briefly reported previously [5], Mo(O)$_2$mes$_2$ reacts with CO (3 atm) in neat pyridine to give dimesityl ketone **1** (5% yield) along with a dihydropyridine dimer **2**, 1,1′-bis(mesitoyl)-1,1′,4,4′-tetrahydro-4,4′-bipyridine (25% yield), and trace amounts of bimesityl.



Because the identification of **2** was made on the basis of spectroscopic grounds that did not reveal the stereochemistry of the molecule, an X-ray structural determination was carried out. An ORTEP view of the molecular structure of **2** is shown in Fig. 1, and some selected bond distances and angles are listed in Table 1. The most notable features are as follows: (a) the carbonyl groups are *trans* to each other,

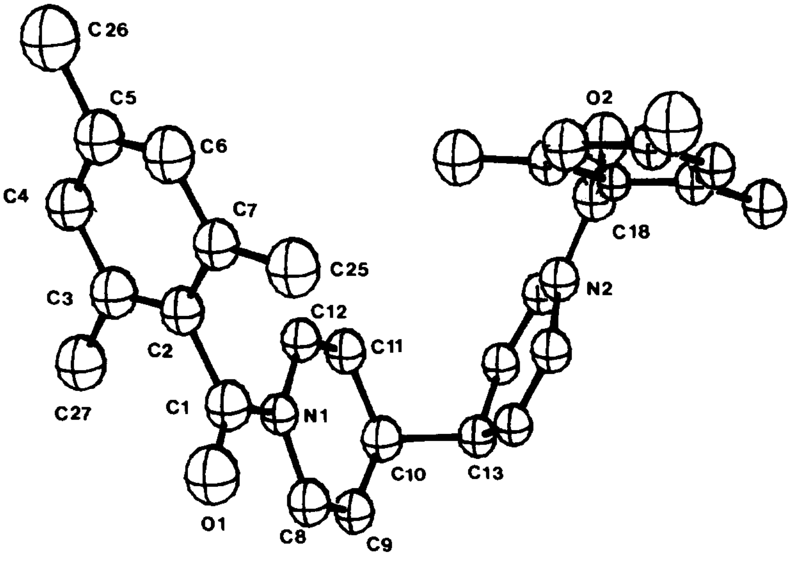


Fig. 1. Molecular structure and atom labelling of **2**.

Table 1

Selected bond lengths (Å) and bond angles (deg) for **2** (mean values)

N(1)-C(1)	1.40(2)	C(9)-C(10)	1.49(2)
N(1)-C(12)	1.40(2)	C(11)-C(12)	1.35(4)
N(1)-C(8)	1.43(0)	C(8)-C(9)	1.33(1)
C(10)-C(13)	1.65(2)	C(1)-C(2)	1.51(2)
C(2)-C(7)	1.43(4)	C(4)-C(5)	1.36(1)
C(6)-C(7)	1.41(1)	C(5)-C(26)	1.47(1)
C(3)-C(27)	1.54(2)	C(7)-C(25)	1.54(2)
C(1)-O(1)	1.28(1)		
C(1)-N(1)-C(8)	118.5(5)	N(1)-C(1)-O(1)	118.4(2)
C(1)-N(1)-C(12)	122.0(1)	O(1)-C(1)-C(2)	120.0(2)
C(2)-C(1)-N(1)	120.0(2)	C(8)-N(1)-C(12)	119.5(2)

each of them lying almost in the same plane as its neighbouring pyridyl group; (b) in each half of the molecule, the pyridyl and the mesityl groups are almost perpendicular to one another; the values of the relevant angles are 75 and 81°; (c) the pyridyl groups are facing but are not parallel to each other, with a dihedral angle of 136°.

Influence of experimental conditions

When the reaction is performed under 40 atm instead of 3 atm of CO increased amounts of both ketone and amide are observed; this effect is more pronounced for **1** than for **2** (Table 2). Increasing the temperature from 20 to 70 °C has a very large effect on the ratio of **1** to **2** which increases markedly (Table 2). IR monitoring of these reactions also shows that there are strong absorptions in the range 1800 to 2060 cm^{-1}, indicating the presence of molybdenum carbonyl species. Although it might be possible to separate these complexes by column chromatography we cannot suggest structures for them, but they are certainly a mixture of different polynuclear species containing terminal and bridged oxo groups. These complexes certainly arise from the interaction of CO with reduced molybdenum species produced through the reductive elimination process leading to **1** [6*].

Table 2

Reactions of CO and $Mo(O)_2mes_2$

Temperature (°C)	P(CO) (atm)	Solvent	**1** (%) [a]	**2** (%) [a]
20	3	C_5H_5N	5	25
20	40	C_5H_5N	14	31
70	3	C_5H_5N	24	16
20	3	THF	< 2	0
20	3	THF [b]	19	0
20	3	THF [c]	37	0

[a] Based on Mo. [b] 2 equiv. pyr/Mo. [c] 4 equiv. pyr/Mo.

---

* Reference number with an asterisk indicates a note in the list of references.

Table 3

Reactions of CO and $Mo(O)_2mes_2$ in the presence of methyl pyridines

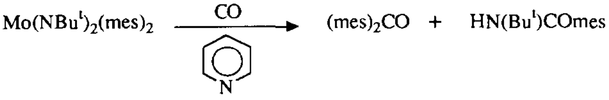
Me-pyridine	Temperature (°C)	**1** (%)	dihydropyridine dimer (%)
2-Me	60	39	0
3-Me	20	4	3
4-Me	20	2	10

Another interesting observation concerns the carbonylation reactions in THF solutions in the absence of pyridine or the presence of variable amounts of it. When the reaction is carried out in neat THF, almost total decomposition of $Mo(O)_2mes_2$ is observed and $< 2\%$ of **1** is formed. In the presence of 2 or 4 equivalents of pyridine/Mo, the amounts of **1** are higher, namely 19 and 39% respectively, and no dihydropyridine dimer is detected under these conditions.

Experiments conducted in neat picolines revealed the influence of substitution on the pyridine ring. At room temperature under 3.5 atm CO, both 3- and 4-methylpyridines afford **1** and the corresponding dihydropyridine dimers in very low yields (Table 3). Because of the low solubility of $Mo(O)_2mes_2$ in 2-methyl pyridine, the reaction must be carried out under more forcing conditions (60 °C). Under these conditions, no dihydropyridine dimer could be detected, whereas up to 39% of **1** was obtained. These results are indicative of steric rather than electronic effects. This is particularly evident for 2-methylpyridine, for which the need to use a higher temperature and the effect of steric hindrance would disfavour formation of dihydropyridine dimer.

Carbonylation of $Mo(N^tBu)_2mes_2$

In order to get a better insight into the *N*-acylation of pyridine with CO and d^0 molybdenum complexes we thought it appropriate to compare the reactivities of $Mo(O)_2mes_2$ and the isoelectronic $Mo(N^tBu)_2mes_2$. Exposure of stirred yellow pyridine solutions of the diimido complex to 3 atm of carbon monoxide at room temperature resulted in an instantaneous change in colour, and the green solution formed turned rapidly to dark green. Analysis of the black residue left after pyridine evaporation revealed the presence of dimesitylketone (60%) along with mesityl(tert-butyl)amide $HN(^tBu)COmes$ (40%). The dihydropyridine dimer **2** could not be isolated or spectroscopically detected.



It is noteworthy that this reaction proceeds also under an atmospheric pressure of CO, and even below 20 °C. Analysis of the results of experiments run under normal pressures of CO indicates that the ratio of the ketone to the amide is unaffected by change in this pressure.

As in the case of experiments at 70 °C with $Mo(O)_2mes_2$ in pyridine, IR spectroscopy reveals the presence of molybdenum carbonyl complexes. However, all attempts to obtain these species in a form pure enough for structural studies have failed, and their apparent polynuclearity has prevented accurate elemental analysis.

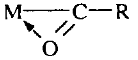
Mechanistic considerations

The main points arising from this study are as follows: (i) the unprecedented formation of a dihydropyridine dimer from CO and pyridine in the presence of $Mo(O)_2mes_2$; (ii) the important difference in behaviour between $Mo(O)_2mes_2$ and $Mo(N^tBu)_2mes_2$, formation of **2** occurring only in the case of the dioxo complex, the latter being far more reactive than the former.

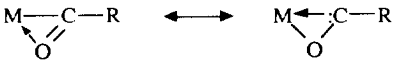
Although the formation of dimesityl ketone from both complexes is remarkable in itself, since it occurs with d^0 complexes, it can be evidently accounted for in terms of reductive elimination, for which there is a precedent in the literature [7]. On the other hand, formation of dihydropyridine dimers represents the first example of a new type of a metal-mediated carbonylation reaction, which can be described as a reductive *N*-acylation of pyridine by carbon monoxide mediated by a high-valent molybdenum oxo complex.

In the absence of isolated or spectroscopically characterised intermediates it is not easy to decide between the possible mechanisms which might lead to the *N*-acylation and the reductive coupling of the pyridine ring, given the fact that the reaction is multistep. However, in light of the above results and of literature reports we think it is reasonable to propose some tentative explanations, as follows. Obviously the common key step of the carbonylation chemistry described in this work is the initial coordination of a molecule of CO, leading to an unstable d^0 carbonyl species. It is important to note that in the reaction of $Mo(O)_2mes_2$ with CO the pyridine plays a pivotal role as a ligand in stabilizing the complex and also raising the electron density on the electrophilic molybdenum atom. Reactions in THF in the absence of pyridine illustrate the effect of pyridine, since formation of dimesityl ketone occurs only in its presence. Recently, examples of cases in which the choice of solvents is the key to formation of carbonylation products have been described [8]. Furthermore, only when the ratio pyridine/Mo is higher than 30 is formation of the dihydropyridine dimer observed. In the absence of any possibility of oxidatively-promoted or Lewis acid assisted migration [9], it is conceivable that since the CO ligand cannot π-bond strongly to the molybdenum(VI) species the migration of a mesityl would be enhanced, giving rise to a metal-acyl complex. The reactions of this species will then determine the final products of the reaction.

It is now well documented that in coordination to electron-deficient transition metals the acyl group adopts an η^2-binding mode in which the oxygen atom is strongly bound to the metal center [10]:



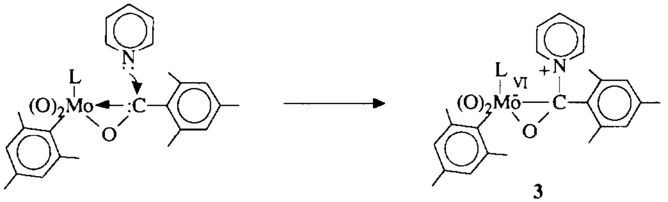
This type of bonding seems to us to provide the most likely explanation of the formation of the dihydropyririne dimer. Indeed, it has been shown that η^2-acyl species show a reactivity pattern which can be attributed to their substantial oxycarbenoid/carbenium character [11]:



Examples of the special reactivity of η^2-acyl complexes arising from the highly electrophilic character of the acyl carbon atom of this ligand are provided by several unusual reactions. Thus the oxycarbene resonance structure has been invoked to account for reactions such as formation of metal-bound enolates or enediolates, acyl Cα deprotonation, ketone ligand formation, reductive CO coupling, and reactions with nucleophiles [11b,c,d,12].

As we pointed out above, most examples of transition-metal η^2-acyl complexes involve d^0 Group IV elements or other oxophilic metals, although a number of Group VI η^2-acyl complexes are known [9,10d–i]. However, the range of chemistry of molybdenum η^2-acyl reagents has not yet been established. We believe that the example we describe in this study might relate to molybdenum η^2-acyl complexes. The existence of an η^2-acyl structure with an important oxycarbene character could be understood in terms of high oxygen affinity and high coordinative unsaturation of $Mo(O)_2mes_2$.

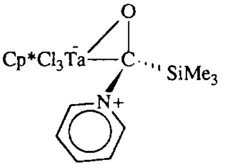
Although it has not been possible to isolate the postulated dioxo molybdenum η^2-acyl species the results we have obtained can reasonably be explained in terms of the intermediacy of such a species. The resulting carbenoid character of the mesitoyl ligand provides a basis for understanding the next step in the formation of dihydropyridine **2**, since nucleophilic attack by a pyridine molecule on the electrophilic carbon atom of the mesitoyl ligand would afford a pyridinium-type adduct:

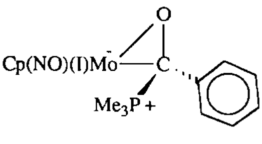


3

L = Pyridine

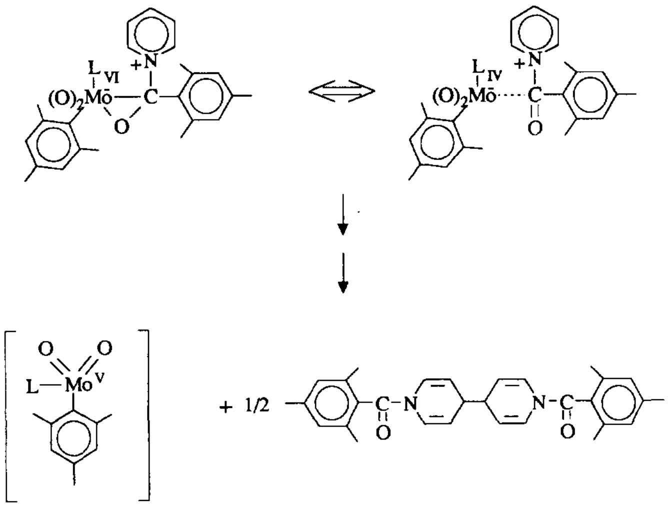
There are precedents for adducts of this type, involving tantalum and molybdenum η^2-acyl complexes and Lewis bases such as pyridine [12a] and trimethylphosphine [13], respectively:





The fate of this kind of adduct would then depend of different factors. It could be stable enough to be isolated as in the case of the tantalum and molybdenum cyclopentadienyl species mentioned above or be transformed to more stable compounds, as in the case of **3**. It is possible that in pyridine under CO adduct **3** might be stable, because NMR monitoring of reactions in C_5D_5N and examined under a CO atmosphere does not reveal the presence of dihydropyridines which are observed only after release of the CO and work-up involving non-polar solvents [14*].

The formation of **2** from the pyridinium complex **3** may involve reductive C–C coupling at the 4 position of the pyridine ring [16*], as shown in the following simplified scheme:



L = Pyridine

This final reaction step shows some analogy to the reductive coupling of a pyridine ring caused by a titanium phenoxy η^2-iminoacyl compound [17]. However, in the absence of isolation or unambiguous spectroscopic characterisation of intermediates, an attempt to decide between all the possible mechanisms which might involve transient pyridinyl radicals or a concerted electron transfer process would be wholly speculative.

The fact that no dihydropyridine dimer is formed in the case of $\mathrm{Mo(N^tBu)mes_2}$ under the conditions used for $\mathrm{Mo(O)_2mes_2}$ could be attributed to the better π-donating properties of the imido ligand [18], which makes the molybdenum atom less electrophilic. Extended Hückel calculations have shown that the positive net charge on the molybdenum is much higher for a dioxo complex than for a diimido species [19*]. Accordingly there would be an important reduction of the carbenoid character of the carbonyl group in the mesitoyl ligand arising from the interaction of CO with $\mathrm{Mo(N^tBu)_2mes_2}$, and in consequence the reaction of this acyl complex would follow an entirely different course. No pyridine attack on the acyl carbon atom would occur and reductive elimination would give dimesityl ketone as the major product. The difference in behaviour between the dioxo and the diimido complexes arising from electron density differences at molybdenum also gains support from the influence of pyridine in the carbonylation. Indeed, although there is no influence of the solvent in the case of $\mathrm{Mo(N^tBu)_2mes_2}$, the reaction having the same course either in pyridine or other solvents, the situation is different with $\mathrm{Mo(O)_2mes_2}$. Recently, a comparative study of isoelectronic nitrido, imido and oxo complexes of osmium(VI) has shown differences in reactivity between imido and oxo species comparable to those observed in this work. These differences in reactivity with CO of the oxo and imido osmium complexes have been related to the relative strength of metal–heteroatom bond [20].

The production of mesityl(tert-butyl)amide (ca 40%) as the other product of the carbonylation reaction of $Mo(N^tBu)_2mes_2$ is not unprecedented. Wilkinson et al. reported that interaction of CO with chromium or molybdenum di(tert-butylimido) dimesityl affords mesityl(tert-butyl)amide, and they suggested as an intermediate a carboxamide derivative arising from migration of an acyl group to an imido nitrogen function [3].

Production of the amide necessitates a hydrogen source, and since hydrogen might be abstracted from the methyl groups of the mesityl ligands as recently suggested [3,21], we performed the carbonylation reaction with $Mo(N^tBu)_2mes_2$ 50% deuterated on the methyl groups of the mesityl ligands. Mass spectroscopy and IR spectroscopic analysis showed total absence of deuterium in the amido group of the amide formed in the reaction, ruling out hydrogen abstraction from the methyl groups of the mesityl ligands.

Another plausible explanation involves possible hydrolysis of the putative carboxamido or oxazamolybdenacycle intermediates during the chromatographic workup, as observed in the reaction of isocyanates with dioxo or diimido molybdenum(VI) complexes [22].

Experimental

^1H and ^{13}C NMR spectra were recorded on a Bruker AM-200 spectrometer and IR spectra on a FT-IR Nicolet MX-S instrument. Elemental analyses were carried out by the Service Central d'Analyses CNRS. All manipulations were carried out under purified N_2 by standard Schlenk techniques. Toluene, n-pentane and diethyl ether were distilled from sodium benzophenone ketyl. Pyridines were distilled from CaH_2 under N_2 and stored under N_2.

The compounds $Mo(O)_2mes_2$ [23] and $Mo(N^tBu)_2mes_2$ [3] were prepared previously described.

Preparation of partially deuterated $Mo(N^tBu)_2mes_2$ *[24].* 9.1 g (45.7 mmol) of 2-bromomesitylene was treated with 0.27 g (11.2 mmol) of sodium hydride in 15 ml (212.5 mmol) of DMSO-d_6. After 4 days' refluxing under N_2, distilled water was added at 0 °C, the mixture was extracted with Et_2O, and the organic phase dried over $MgSO_4$. Distillation of the crude product under vacuum (64 °C, 2 mmHg) yielded 6.8 g of 2-bromomesitylene 50% deuterium-labeled in the methyl groups as revealed by ^1H NMR spectroscopy. Preparation of deuterated $Mo(N^tBu)_2mes_2$ was then carried out by the method used for the undeuterated species [3].

Apparatus and methods for the CO reaction

Reactions were carried out in 3-oz Lab-Crest (Fischer–Porter) glass pressure reaction vessels, or for experiments conducted at pressures higher than 10 atm, in a rocking Prolabo autoclave. In a typical experiment a solution of the complex in the appropriate solvent was introduced under N_2 into the pressure reaction vessel. The mixture was cooled to -60 °C, the vessel was evacuated, and then immediately pressurized up to the appropriate CO pressure. Reactions with $Mo(O)_2mes_2$ were carried out for 48 h, whereas those with $Mo(N^tBu)_2mes_2$ were left under CO overnight, although reaction of the diimido complex took place immediately as indicated by the colour change. The CO was released and the contents of the reaction vessel transferred to a Schlenk tube. After removal of the solvent in vacuum the residue was dissolved in a minimum of CH_2Cl_2 and chromatographed under nitrogen on a silica gel column.

X-ray data collection and structure solution of **2**

Compound **2** crystallized in the monoclinic space group $P2_1/c$ with $a = 17.25$ (3), $b = 7.75$ (2), $c = 20.37$ (2) Å; $\beta = 108.8$ (5)°, and $V = 2578.9$ Å^3; $D_c = 1.18$ g cm^{-3}; $M_r = 582.55$, $Z = 4$, $\mu = 0.7$ cm^{-1}.

A crystal of size 0.3 × 0.2 × 0.2 mm obtained from THF/Et_2O at 0 °C was protected by silicone oil and mounted on an Enraf-Nonius CAD4 diffractometer equipped with a monochromator for Mo-K_α radiation ($\lambda = 0.7107$ Å), θ max = 19 °.

Table 4

Positional parameters with their estimated standard deviations in parentheses

Atom	x	y	z	B (Å^2) [a]
N1	0.8558(6)	0.178(2)	0.2600(7)	3.5(3)
N2	0.6731(6)	0.605(2)	0.3248(7)	2.9(3)
O1	0.8569(6)	0.015(2)	0.1497(7)	5.0(3)
O2	0.6524(6)	0.897(2)	0.3306(7)	5.9(3)
C1	0.8674(8)	0.162(2)	0.1836(9)	4.1(4)
C2	0.8865(7)	0.321(2)	0.1465(8)	2.1(3)
C3	0.9522(8)	0.335(2)	0.1429(9)	3.1(3)
C4	0.9694(8)	0.487(2)	0.1062(9)	3.1(4)
C5	0.9207(8)	0.611(2)	0.0724(9)	3.3(4)
C6	0.8529(8)	0.588(2)	0.0758(9)	4.1(4)
C7	0.8359(8)	0.442(2)	0.1117(9)	3.4(4)
C8	0.8712(8)	0.340(2)	0.3024(9)	3.5(4)
C9	0.8560(7)	0.360(2)	0.3717(9)	3.2(4)
C10	0.8215(8)	0.230(2)	0.4077(9)	3.3(4)
C11	0.8179(8)	0.059(2)	0.3644(9)	3.3(4)
C12	0.8372(8)	0.037(2)	0.2975(9)	3.3(4)
C13	0.7425(8)	0.287(2)	0.4032(9)	3.8(4)
C14	0.7442(8)	0.458(2)	0.4444(9)	3.5(4)
C15	0.7140(8)	0.603(2)	0.4093(9)	3.9(4)
C16	0.6654(8)	0.447(2)	0.2806(9)	3.3(4)
C17	0.6950(8)	0.304(2)	0.3146(9)	3.6(4)
C18	0.6413(8)	0.754(2)	0.291(1)	4.3(4)
C19	0.5861(8)	0.743(2)	0.2068(9)	3.9(4)
C20	0.5219(8)	0.697(2)	0.199(1)	4.5(4)
C21	0.4699(9)	0.688(2)	0.121(1)	4.4(4)
C22	0.4885(9)	0.734(2)	0.053(1)	4.9(4)
C23	0.5535(9)	0.786(3)	0.060(1)	5.1(5)
C24	0.6081(8)	0.797(2)	0.138(1)	4.1(4)
C25	0.7599(9)	0.415(3)	0.113(1)	5.1(4)
C26	0.938(1)	0.764(3)	0.031(1)	5.8(5)
C27	1.0093(8)	0.205(2)	0.1809(9)	4.0(4)
C28	0.501(1)	0.652(3)	0.273(1)	5.3(5)
C29	0.432(1)	0.727(3)	−0.033(1)	6.7(6)
C30	0.6779(9)	0.856(3)	0.148(1)	5.4(5)

[a] All atoms were refined isotropically.

Only 989 unique reflections with $I > 3\sigma(I)$ were used in the structure determination. A linear correction was used because of a 12% loss of intensity. The structure was determined by direct methods (MULTAN) [25] using SDP software [26] and completed by the difference Fourier method. H atoms were introduced at idealized position in the calculation before the last refinement cycles but not refined. Full least-squares refinement included isotropic thermal parameters for non H-atoms. A final difference Fourier synthesis did not reveal any peak of density > 0.22 e Å^{-3}. $R = 0.09$ and $R_w = 0.11$, $w = 1/\sigma^2$ (σ = estimated standard deviation on intensity). The non-hydrogen atom coordinates are listed in Table 4. Lists of hydrogen atom coordinates, thermal parameters, and structure factors, and a complete table of bond lengths and angles are available from the authors.

Acknowledgements

We thank Dr. M. Pierrot for the X-ray structure determination and Dr. M. Razjmann for his help with the extended Hückel calculations.

References and notes

1 P. Pino, F. Piacenti and M. Bianchi, in I. Wender and P. Pino (Eds.), Organic Synthesis via Metal Carbonyls, Vol. II, Wiley-Interscience, New York, 1977, p. 278; I. Tkatchenko, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, 1982, Chap. 50, p. 173.

2 F.M. Su, C. Cooper, S.J. Geib, A.L. Rheingold and J.M. Mayer, J. Am. Chem. Soc., 108 (1986) 3545.

3 A.C. Sullivan, G. Wilkinson, M. Motavelli and M.B. Hursthouse, J. Chem. Soc., Dalton Trans., (1988) 53.

4 H.G. Alt and H.I. Hayen, Angew. Chem., Int. Ed. Engl., 24 (1985) 497.

5 R. Laï, S. Le Bot and R. Faure, J. Organomet. Chem., 336 (1987) C5.

6 It was checked in experiments run at 70 °C, that the production of reduced molybdenum species could not arise from the interaction of CO with the oxo groups since chromatography and chemical analysis did not reveal the presence of CO_2.

7 M. Vivanco, J. Ruiz, C. Floriani, A. Chiesi-Villa and C. Guastini, Organometallics, 9 (1990) 2185 and refs. therein.

8 T.Y. Meyer, L.R. Garner, N.C. Baenziger and L. Messerle, Inorg. Chem., 29 (1990) 4045.

9 M.D. Curtis, K.-B. Shiu and W.M. Butler, J. Am. Chem. Soc., 108 (1986) 1550 and refs. therein.

10 (a) J.P. Collman, L.S. Hegedus, J.R. Norton and R.G. Finke, in Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, 1987, p. 108; (b) G. Cardaci, G. Bellachioma and P. Zanazzi, Organometallics, 7 (1988) 172 and refs. therein; (c) L.D. Durfee and I.P. Rothwell, Chem. Rev., 88 (1988) 1059; (d) H.G. Alt, J. Organomet. Chem., 127 (1977) 349; (e) E. Carmona Guzman, G. Wilkinson, R.D. Rogers, W.E. Hunter, M.J. Zaworotko and J.L. Atwood, J. Chem. Soc., Dalton Trans., (1980) 229; (f) E. Carmona, L. Sanchez, J.M. Marin, M.L. Poveda, J.L. Atwood, R.D. Priester and R.D. Rogers, J. Am. Chem. Soc., 106 (1984) 3214; (g) F.R. Kreissl, W.J. Sieber, H. Keller, J. Riede and M. Wolfgruber, J. Organomet. Chem., 320 (1987) 83; (h) E. Carmona, M.A. Munoz and R.D. Rogers, Inorg. Chem., 27 (1988) 1598; (i) C.A. Rusik, M.A. Collins, A.S. Gamble, T.L. Tonker and J.L. Templeton, J. Am. Chem. Soc., 111 (1989) 2250.

11 (a) K. Tatsumi, A. Nakamura, P. Hofmann, P. Stauffert and R. Hoffmann, J. Am. Chem. Soc., 107 (1985) 4440; (b) P.T. Wolczanski and J.E. Bercaw, Acc. Chem. Res., 13 (1980) 121; (c) K.G. Moloy, P.J. Fagan, J.M. Manriquez and T.J. Marks, J. Am. Chem. Soc., 108 (1986) 56; (d) B.D. Martin, S.A. Matchett, J.R. Norton, O.P. Anderson, J. Am. Chem. Soc., 107 (1985) 7952.

12 (a) J. Arnold, T.D. Tilley and A.L. Rheingold, J. Am. Chem. Soc., 108 (1986) 5355; (b) J. Arnold, T.D. Tilley, A.L. Rheingold, S.G. Geib and A.M. Arif, J. Am. Chem. Soc., 111 (1989) 149.

13 P.V. Bonnesen, P.K.L. Yan and W.H. Hersh, Organometallics, 6 (1987) 1587.

14 Attempts to obtain indirect evidence for the intermediacy of 3 by treating the resulting red brown pyridine solution, after CO release, with $NaBH_4$, Zn, or Grignard reagents [15] were unsuccessful.

15 R.M. Acheson, in An Introduction to the Chemistry of Heterocyclic Compounds, Interscience, New York, 1962; A. Eisner and J. Kuthan, Chem. Rev., 72 (1972) 1.

16 The nature of the molybdenum complex present at the end of the reaction is yet not known. The insolubility in most solvents of the red-brick solid isolated from the reaction mixtures precluded purification and thus accurate elemental analysis. However, because of its low solubility and from IR and analytical data, we think it may be a polymeric mesityl- and pyridine-containing molybdenum species with terminal and μ-oxo bonds.

17 L.D. Durfee, P.E. Fanwick and I.P. Rothwell, J. Am. Chem. Soc., 109 (1987) 4720.

18 W.A. Nugent and J.M. Mayer, In Metal–Ligand Multiple Bonds, Wiley-Interscience, New York, 1988.

19 Extended Hückel calculations on two model molecules $Mo(O)_2(C_6H_5)_2$ and $Mo(NMe)_2(C_6H_5)_2$ gave 3.23 and 2.32 as positive net charge values on molybdenum, respectively (R. Laï, M. Rajzmann and F. Djafri, to be published).

20 R.W. Marshman and P.A. Shapley, J. Am. Chem. Soc., 112 (1990) 8369.

21 A. Gutierez, G. Wilkinson, B. Hussain-Bates and M.B. Hursthouse, Polyhedron, 9 (1990) 2081.

22 R. Laï, S. Mabille, A. Croux and S. Le Bot, Polyhedron, in press.

23 B. Heyn and R. Hoffmann, Z. Chem., 16 (1976) 195.

24 K.H. Theopold, J. Silvestre, E.K. Byrne and D.S. Richeson, Organometallics, 8 (1989) 2001.

25 P. Main, L. Lessinger, M.M. Woolfson, G. Germain and J.P. Declercq, MULTAN 77. A system of Computer Programs for the Automated Solution of Crystal Structures from X-ray Diffraction Data. Univs. of York, England and Louvain-la Neuve, Belgium, 1977.

26 B.A. Frenz, in H. Schenk, R. Olthof-Hazelkamp, H. van Koningsveld and G.C. Bassi (Eds.), Computing in Crystallography, Delft Univ. Press, 1978, p. 64–71.