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Review

Trimethyl phosphine complexes of molybdenum and tungsten containing dinitrogen, ethylene, carbon dioxide and related ligands

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I first became involved in Organometallic Chemistry in the mid-seventies, after a three-year post-doctoral stay at Imperial College, under the supervision of Prof. G. Wilkinson. In those days (as in earlier and later times) there was a great deal of activity in Wilkinson's laboratories, and I had the opportunity to learn a lot about chemistry and to enjoy fully the excitement of synthetic work aimed at the study of elusive organometallic molecules. My work at Imperial College concentrated primarily on alkyl and hydride complexes of transition metals (mainly manganese, molybdenum, and tungsten). I returned to Sevilla at the end of September 1977, to take up a temporary lectureship in Inorganic Chemistry, bringing with me some ideas for starting research and quite a lot of material which I had either bought or had made available to me thanks to the generosity of my former supervisor.

The work started at Sevilla has dealt mainly with nickel, molybdenum, and tungsten chemistry. The initial approach to the study of the $Mo-N_2-PMe_3$ system, was induced by Karsch's report [1] on the synthesis of *cis*-$[Cr(N_2)_2(PMe_3)_4]$, and by the rather surprising absence of compounds of this type among the long series of dinitrogen complexes that had been thoroughly studied by Chatt [2] and his coworkers at Sussex. The first experiments were made at Imperial College a few months before my departure, and since the results were rather encouraging, and since I was deeply involved in other studies on the chemistry of hydride and alkyl complexes of molybdenum, I thought that the $Mo-N_2-PMe_3$ system could be a good starting point back in Sevilla.

The work carried out at Sevilla developed very slowly, not only because of my own limitations and insufficient experience, but also because of the lack of experimental facilities and the heavy teaching and administration duties I carried in those days. Illustrative of the equipment difficulties is the fact that until mid-1983, no NMR facilities were available except for an old Perkin–Elmer R12 spectrometer, which was nevertheless, most valuable for our research. In this review I present an account of the work carried out by my group on the chemistry of molybdenum and tungsten complexes containing coordinated N_2, C_2H_4, CO_2 and related molecules. In addition to already published work I include some recent results that have

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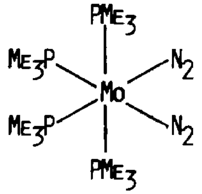
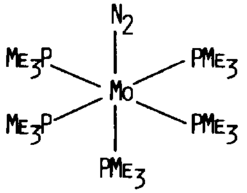
recently been submitted for publication or will be submitted shortly. Some of the compounds described in the following sections have been independently prepared and characterized by Green and coworkers [3].

Dinitrogen complexes. The sodium amalgam reduction of $[MoCl_3(PMe_3)_3]$ carried out in tetrahydrofuran (thf), under N_2, produces a red-orange crystalline material as the only isolable product. This complex was initially formulated [4] as *trans*-$[Mo(N_2)_2(PMe_3)_4]$, on the basis of the initial analytical and spectroscopic data. It soon became evident that this formulation was incorrect, and further studies revealed that this compound, and its tungsten analogue, must be formulated as "$MCl(N_2)(PMe_3)_4$". An investigation of their chemical properties demonstrated that they behave as equimolar mixtures of $[MCl_2(PMe_3)_4]$ and $[M(N_2)_2(PMe_3)_4]$ [5].

It was rather surprising, though interesting and rewarding, to find that when the above reduction was carried out under the same experimental conditions, but using dispersed sodium instead of sodium amalgam, the *cis* isomer, *cis*-$[Mo(N_2)_2(PMe_3)_4]$ (I) was obtained instead. It was noted [6] that the nature of the reducing agent is important, not only because it determines the composition of the dinitrogen complexes but also because it makes work up of the reaction mixture easier. In this respect, it should also be pointed out that use of different crops of the starting material, $[MoCl_3(thf)_3]$, obtained from different preparations, may sometimes have a considerable influence in the course of the reaction. The investigation of the chemistry of these dinitrogen complexes was part of the PhD Thesis of José M. Marín, it was later completed by Rafael Alvarez, and extended to the analogous tungsten system by Agustín Galindo [7,8]. Manuel L. Poveda, who was the recipient of the first PhD Thesis on Organometallic Chemistry at the University of Sevilla, provided an important contribution to the developing of this chemistry as well as to that of the nickel alkyl and acyl complexes we were simultaneously investigating. Some of the reactions of complex I that have been studied are shown in Scheme 1. Of these, I will briefly discuss now the reactions with phosphine ligands, leaving those with C_2H_4 and CO_2 to subsequent sections.

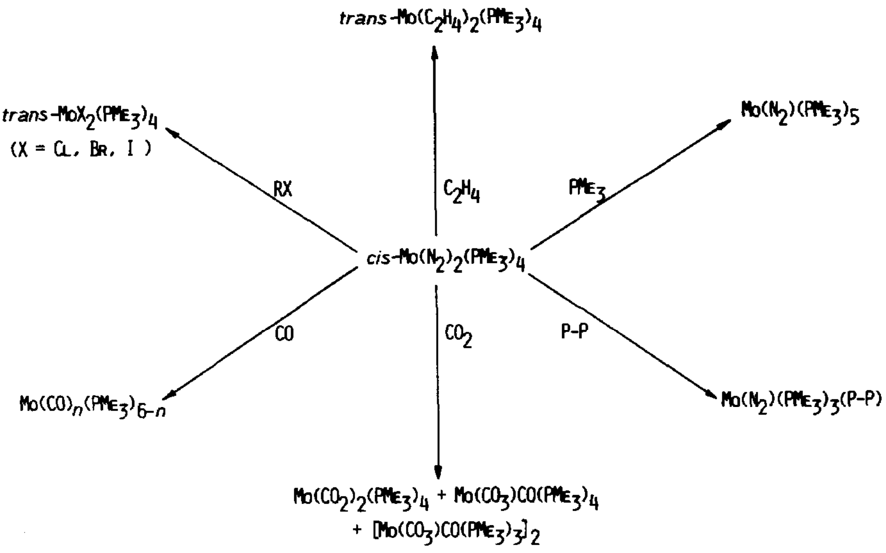


(I)



(II)

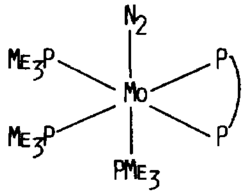
The compound $[Mo(N_2)(PMe_3)_5]$ (II), was accidentally discovered during attempts to prepare a bis(propylene) complex analogous to *trans*-$[Mo(C_2H_4)_2(PMe_3)_4]$. A yellow solid displaying a strong absorption at 1950 cm^{-1} and ^1H and ^{31}P NMR spectral properties [6] characteristic of a MP_5 unit, was obtained instead. The compound was subsequently prepared in very high yields by the reaction of I with PMe_3, as shown in Scheme 1. The ease with which complex I reacts with CO_2, along with the influence exerted by the phosphine co-ligands on the course of this reaction, has stimulated work in our group aimed at the preparation of related dinitrogen complexes. Some of the systems investigated are shown in Scheme 1. For



Scheme 1.

instance, complexes of the type $[Mo(N_2)(PMe_3)_3(P{-}P)]$, where $P{-}P = Me_2P(CH_2)_n PMe_2$ ($n = 1$, dmpm; $n = 2$, dmpe), can be obtained by the room temperature reaction [9] of I with the chelating phosphine ligand, according to eq. 1. These derivatives have $\nu(N{\equiv}N)$ at ca. 1950 cm^{-1}, and show spectroscopic properties fully consistent with their formulation as in III.

$$cis\text{-}[Mo(N_2)_2(PMe_3)_4] + P{-}P \xrightarrow{Ar,\ 20\,°C} [Mo(N_2)(PMe_3)_3(P{-}P)] + PMe_3 + N_2$$
$$(P - P = \text{dmpm, dmpe}) \qquad (1)$$

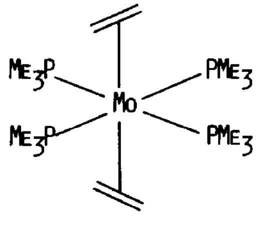


(III)

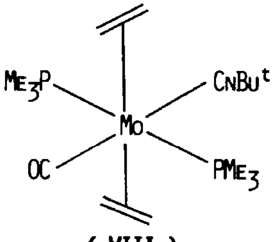
Recent studies [10] carried out by Pedro J. Pérez, based on the more basic and bulkier PEt_3 ligand, which are still in a preliminary stage, show formation of the tris-dinitrogen complex *mer*-$[Mo(N_2)_3(PEt_3)_2]_2(\mu\text{-}N_2)$ from the room temperature reduction of $[MoCl_4(PEt_3)_2]$, under 2–3 atm of N_2, as shown in eq. 2. Related species have been recently described by Richards and co-workers at Sussex [11].

$$[MoCl_4(PEt_3)_2] + PEt_3 \xrightarrow{Na\text{-}Hg,\ N_2} mer\text{-}[Mo(N_2)_3(PEt_3)_2](\mu\text{-}N_2) \qquad (2)$$

The ethylene complexes, trans-[M(C_2H_4)$_2$(PMe_3)$_4$]. As indicated in the previous section, the *cis*-bis(dinitrogen) complex *cis*-$[Mo(N_2)_2(PMe_3)_4]$ reacts with ethylene at room temperature and pressure to give *trans*-$[Mo(C_2H_4)_2(PMe_3)_4]$ (V) [6]. The tungsten analogue, *trans*-$[W(C_2H_4)_2(PMe_3)_4]$ cannot be obtained by this method, but can be made by sodium amalgam reduction of $[WCl_4(PMe_3)_3]$, under ethylene [7]. A similar reduction procedure can be used by the synthesis of V. Both compounds are amber crystalline materials, very reactive towards oxygen. Structural studies [6,7] show they are essentially octahedral, with the ethylene molecules staggered with respect to one another and eclipsing the corresponding *trans*-P–M–P vectors of the equatorial plane. Both compounds display a rich chemistry, which is summarized in Scheme 2 for the molybdenum derivative V. The discussion of the reactions with CO_2 and CS_2 is deferred until the following section.



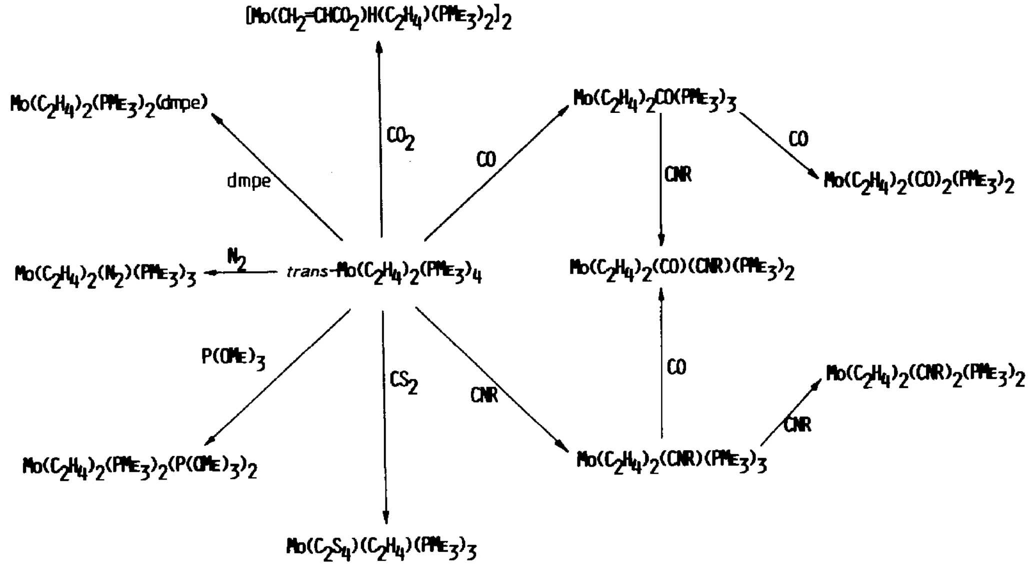
(V)



(VIII)

Compound V has a strong tendency to undergo dissociation of one of its PMe_3 ligands in solution, and this is clearly shown by the facile reaction with N_2 to afford *trans,mer*-$[Mo(C_2H_4)_2(N_2)(PMe_3)_3]$, and with CO to produce the analogous carbonyl derivative, *trans,mer*-$[Mo(C_2H_4)_2CO(PMe_3)_3]$ (VI). No change in the geometrical arrangement of the ethylene ligands takes place, as demonstrated by an X-ray analysis [6] carried out on complex VI. Much to our surprise, the bis-ethylene complexes can be carbonylated under 2–3 atm of CO, with formation of *trans,trans,trans*-$[M(C_2H_4)_2(CO)_2(PMe_3)_2]$, i.e., without displacement of the ethylene ligands [7].

Similar behaviour was later found in the analogous reactions with isocyanides [12], which are also summarized in Scheme 2. Thus, low temperature addition of 1



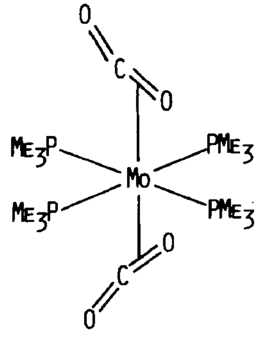
Scheme 2.

equiv. of CNR (R = i-Pr, t-Bu) to petroleum ether solutions of V, affords yellow crystalline materials of composition *trans,mer*-$[Mo(C_2H_4)_2(CNR)(PMe_3)_3]$. These compounds exhibit structures similar to that of VI, as inferred from spectroscopic data. For instance, a broad absorption at ca. 1990–1960 cm^{-1} can be assigned to the C–N stretching frequency of a coordinated isocyanide ligand, while the meridional distribution of the PMe_3 groups is unambiguously indicated by the observation of a doublet (δ 0.9–1.0 ppm) and a triplet (δ 1.0–1.2 ppm) in the ^1H NMR spectrum, and of a pattern characteristic of an AX_2 spin system in the $^{31}P\{^1H\}$ NMR spectrum.

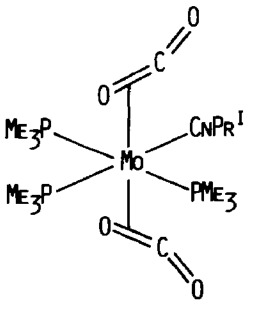
Compounds of the above type have proved difficult to isolate, not only because of their high solubility in normal organic solvents but also because of their tendency to undergo further PMe_3 replacement. Thus, addition of 1 equiv. of CNR to the mono-isocyanide derivatives, or reaction of V with 2 equiv. of CNR, yields yellow crystalline species of composition *trans,trans,trans,*-$[Mo(C_2H_4)_2(CNR)_2(PMe_3)_2]$. As shown in Scheme 2, a number of compounds of the type *trans,trans,trans,*-] $[M(C_2H_4)(PMe_3)_2LL']$ (where $L = L' = CO$ or CNR; $L = CO$, $L' = CNR$; $L = CNR$, $L' = CNR'$) can be prepared starting from the bis ethylene complex V. Spectroscopic data show they have *trans,trans,trans* structures, and this has been confirmed by an X-ray study carried out on compound VIII, the results of which are shown schematically.

Reactions involving CO_2 and CS_2. There has been a great deal of interest in carbon dioxide chemistry in the past decade. This, and the existence at the time we started our work in this area of only a brief report [13] on the reactions of this molecule with dinitrogen complexes of molybdenum, prompted us to investigate its interaction with our dinitrogen compound *cis*-$[Mo(N_2)_2(PMe_3)_4]$ (I). The reaction of I with CO_2 was found to be very complex, and can yield up to four different products depending upon the reaction conditions: yellow $[Mo(CO_2)_2(PMe_3)_4]$ (IX), blue $[Mo(CO_3)CO(PMe_3)_4]$, red $[Mo(CO_3)CO(PMe_3)_3]_2$ and a tetrametallic mixed-valence Mo^{II}–Mo^{V} carbonate structurally characterized as $[Mo_4(\mu_4\text{-}CO_3)(CO)_2(O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OH)_4(PMe_3)_6]$ [14].

Our first report on this reaction [14], mainly concerned the above-mentioned carbonate complexes, since little spectroscopic data were available for IX. Formulation as a head-to-tail dimer seemed in principle more likely in view of the thermal and chemical stability of IX: only mono-CO_2 adducts were known [15–17]; they



(IX)



(X)

were generally unstable, and it was widely accepted that coordination of a second molecule of CO_2 induced additional transformation [18,19]. The scarcity of information of IX was due to our failure to grow single crystals suitable for X-ray studies, and to the lack of NMR facilities in Sevilla in those days.

After this initial report we concentrated on this yellow compound IX, for which several sets of analytical data (C, H, O, P) and a cryoscopic molecular weight determination demonstrated the composition $[Mo(CO_2)_2(PMe_3)_4]$. For this formulation there are several structural possibilities, and although one of my co-workers, M.L. Poveda, intutively proposed the correct one, definite evidence had to be obtained from detailed ^{13}C and ^{31}P NMR studies using compound IX of normal isotopic abundance and of samples enriched in $^{13}CO_2$. These studies were carried out by two good friends, Roberto Sánchez-Delgado in Caracas and David J. Cole-Hamilton, then in Liverpool, and have been described in detail elsewhere [20,21]. From this and from some relevant chemical data [20], for this complex structure IX is proposed.

While we were absolutely convinced that our data led unambiguously to the above structure, it was not an easy task convincing others. As an example of this, publication of these findings was not possible until almost eight months after the original manuscript was received [20]. The previous communication [14] had taken less than four months to appear!.

The structure of IX is very similar to that found for the ethylene complex *trans*-$[Mo(C_2H_4)_2(PMe_3)_4]$ (V), and both compounds exhibit related fluxionality, involving rotation around the metal–olefin or CO_2 bond axis. In addition IX, like V, slowly undergoes dissociation of one of the PMe_3 ligands in solution. In the hope that these similarities might extend to other chemical properties, the reaction of IX with several isocyanides was attempted, and we were very happy to find that these expectations were fulfilled, for new compounds containing coordinated carbon dioxide ligands were formed according to equation 3. The IR spectra of IX and that

$$\textit{trans-}[Mo(CO_2)_2(PMe_3)_4] + CNR \rightarrow \textit{trans,mer-}[Mo(CO_2)_2(CNR)(PMe_3)_3] + PMe_3 \quad (3)$$

$$(R = Me, Pr^i, Bu^t, Cy \text{ and } CH_2C_6H_5)$$

of the $CNBu^t$ derivative, $[Mo(CO_2)_2(CNBu^t)(PMe_3)_3]$ (X) are shown for comparison in Fig. 1. The similarity of the spectra, and in particular the almost exact coincidence of the bands at ca. 1670, 1155 and 1100 cm^{-1}, which are due to the coordinated CO_2 ligands (as demonstrated by isotopic labelling studies), indicate that the substitution reaction occurs without change in the coordination mode of the CO_2 groups.

Single crystals of the isopropyl and benzyl derivatives were grown, and the structures of both compounds determined by X-ray crystallography. After the long delay experienced with the previous publication [20] already referred to, we hurriedly submitted a Chemical Communication [22], but in our rush we incorrectly wrote the formulae of Aresta's [15] and Lappert's [16] CO_2 complexes, that is, of two out of the four [23] known CO_2 complexes! It was not until two weeks later that we realized this mistake and we then rushed a second letter to the Editor in an attempt to correct these formulae before the paper was sent for refereeing (perhaps to the authors whose compounds were incorrectly formulated!). It proved to be too late, and the Editor was kind enough to send us the referees' corrections on a separate

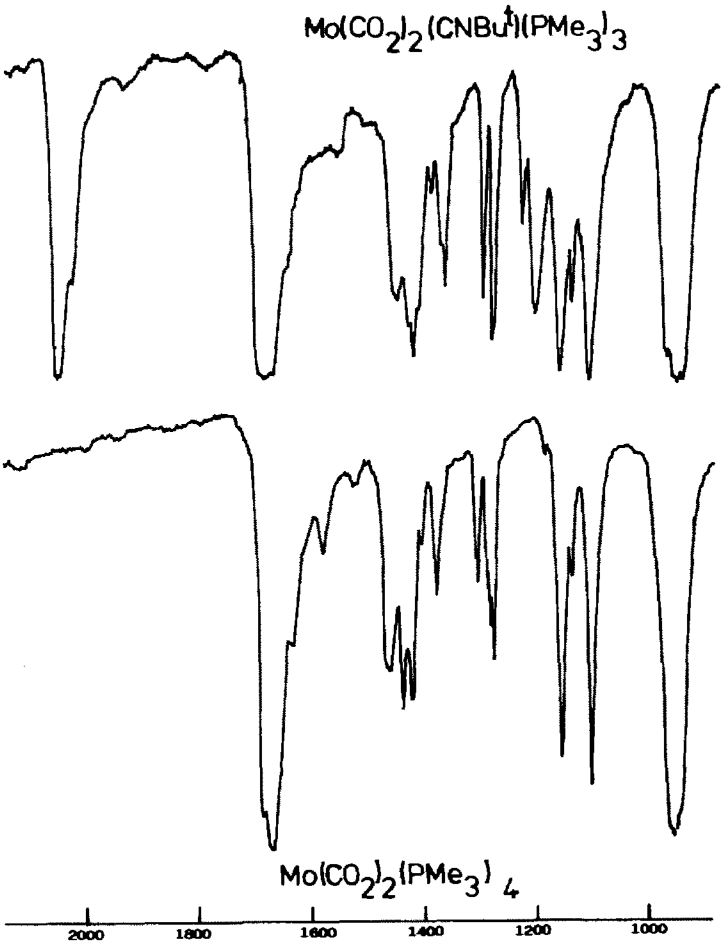


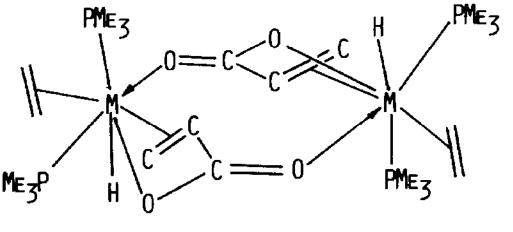
Fig. 1. The spectra of [$Mo(CO_2)_2(PMe_3)_4$] and [$Mo(CO_2)_2(CNBu^t)(PMe_3)_3$].

sheet without including what I assume were not very complementary (though totally justified) remarks on the quality of our proof-reading!.

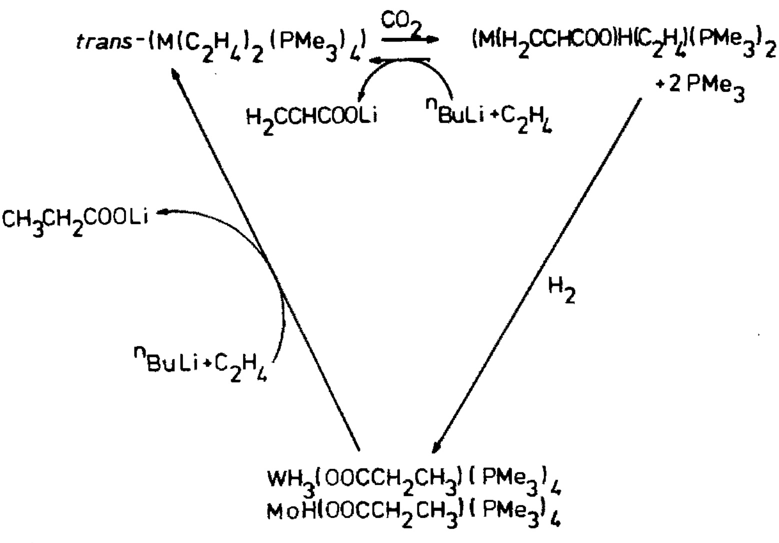
The results of these studies have been fully described elsewhere [21], and revealed strong Mo–CO_2 bonding interactions, with Mo–C bond lengths of ca. 2.10 Å, only slightly longer than the Mo–CNR distance in the same complexes, and appreciably shorter than the Mo–C(ethylene) distances in V and VI. Rather disappointingly, compound IX is fairly unreactive, no reaction being observed in the presence of CH_2N_2, CS_2, SO_2, NO, CN^-, $P(OR)_3$, HBF_4, and other reactants [24]. Also disappointing was our failure to obtain the tungsten-carbon dioxide complexes analogous to IX and X, the reaction of *cis*-[$W(N_2)_2(PMe_3)_4$] with CO_2 yielding only [$W(CO_3)CO(PMe_3)_4$] and [$WH_2(CO_3)(PMe_3)_4$] [25].

A few comments are pertinent at this point on the formation of the carbonato complexes [$Mo(CO)_3)(CO)(PMe_3)_4$] (XI) and [$Mo(CO_3)CO(PMe_3)_3]_2$ (XII). An X-ray analysis carried out on the latter, indicates a structure similar to that found for the PMe_2Ph complex [$Mo(CO_3)CO(PMe_2Ph)_3]_2$, previously characterized by Chatt and co-workers at Sussex [13]. The formation of these disproportionation products in the reaction leading to the bis-adduct IX, raises the question as to when the coordinated CO_2 molecule is sufficiently activated to undergo further transformations. In this respect, it should be pointed out that once $[Mo(CO_2)_2(PMe_3)_4]$ is formed, it is stable towards disproportionation even under the conditions most favourable for the latter reaction [26]. It should also be noted that formation of IX is almost completely prevented by the presence in the reaction mixture of free added PMe_3 (3–4 equiv) or when the reaction is carried out in polar or aromatic hydrocarbon solvents. These observations seem to be consistent with the formation of an intermediate species, "$Mo(CO_2)N_2(PMe_3)_4$" (XIII), which would yield the bis-CO_2 adduct by substitution of N_2 by a second molecule of CO_2, whereas N_2 replacement by solvent or PMe_3 would block the available coordination site at the molybdenum center [20] and activate the coordinated CO_2 through an increase in the backdonation from the metal centre, thus favouring the disproportionation reaction. For this process, metallocyclic head-to-tail dimers, MC_2O_4, are often invoked as intermediates [18,19], but their intermediacy has never been conclusively proved [27]. We believe our disproportionation reaction does not go through a metallocyclic head-to-tail dimer but rather through a non-cyclic species of this type resulting from electrophilic attack by the carbon atom of free CO_2, at the exocyclic oxygen atom of the coordinated CO_2 molecule, so that the process could be viewed formally as an oxide transfer from coordinated to free CO_2 [20]. Some additional comments on this matter will be made at a later stage, in the discussion of the reactions involving carbon disulfide.

The bis(ethylene) complexes *trans*-$[M(C_2H_4)_2(PMe_3)_4]$ can be regarded as electron rich species (or as "high energy" compounds in Green's terms, [28]). This and the availability of a vacant coordination position by facile dissociation of one of the PMe_3 ligands, make these compounds ideal candidates for CO_2 activation. Interaction of the ethylene complexes with CO_2 produces moderately air-stable, crystalline materials, of composition $[M(CH_2CHCO_2H)(C_2H_4)(PMe_3)_2]_2$ (XIV). Evidence that a carbon–carbon bond is formed by coupling of C_2H_4 and CO_2 comes from ^{13}C NMR studies, carried out on a sample ca. 50% enriched in $^{13}CO_2$: of the four resonances, at 32.8, 38.3, 39.6 and 55.1 ppm, attributable to the carbon atoms of the original ethylene molecules, that at 55.1 ppm becomes an approximate 1/2/1 triplet in the spectrum of the enriched sample. Although X-ray studies could not distinguish [29] between formulation of the complexes as hydrido-acrylate or acrylic acid derivatives displaying an agostic-type interaction, recent neutron diffraction studies carried out by Dr. Savariault (CNRS, Toulouse) [30] show them to be the former, as shown in XIV. The reactions considered above, leading to the formation of acrylate and propionate ligands starting respectively from CO_2 and C_2H_4, and from CO_2, C_2H_4 and H_2 (eq. 4 and 5), correspond formally to ethylene



(XIV)



Scheme 3.

carboxylation and hydrocarboxylation, and can be carried out in a cyclic manner, as shown in Scheme 3.

$$CH_2{=}CH_2 + CO_2 \rightarrow CH_2{=}CHCO_2H \tag{4}$$

$$CH_2{=}CH_2 + CO_2 + H_2 \rightarrow CH_3CH_2CO_2H \tag{5}$$

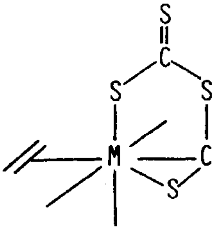
Some final comments are concerned with the reactions of the ethylene complexes with CS_2, which constitute part of the PhD Thesis of Miguel A. Muñoz. With the aim of gaining a deeper understanding of the reaction leading to XIV, we attempted to mimic the formation of acrylate and propionate ligands using related ethylene complexes as starting materials. These include compounds of composition $[M(C_2H_4)_2(PMe_3)_2(P{-}P)]$, (P–P = dmpm, dmpe), $[M(C_2H_4)_2(PMe_3)_2(P(OR)_3)_2]$ (R Me, Et) and other $[M(C_2H_4)_2L_n(PMe_3)_{4-n}]$ derivatives ($n = 1, 2$: L = CO, CNR), but so far all attempts have proved unsuccessful. A different approach involved the investigation of the analogous reaction with CS_2. Not unexpectedly, this reaction takes a different course, but some interesting results have emerged [31] and they will be briefly mentioned below.

Addition of CS_2 to solutions of *trans*-$[M(C_2H_4)_2(PMe_3)_4]$, produces black solids of analytical composition $[M(CS_2)_2(C_2H_4)(PMe_3)_3]$ (XV) according to eq. 6. The distribution of the ethylene and phosphine ligands in the molecules of XV can be

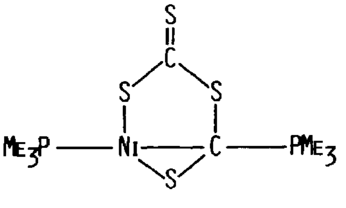
$$trans\text{-}[M(C_2H_4)_2(PMe_3)_4] + 2CS_2 \rightarrow [M(CS_2)_2(C_2H_4)(PMe_3)_3] + C_2H_4 + PMe_3 \tag{6}$$

inferred from ^1H, ^{31}P and ^{13}C NMR data. In addition, there is a sharp IR absorption at 1020 cm^{-1}, which is shifted to 990 cm^{-1} in the spectrum of a $^{13}CS_2$ enriched sample, indicating the presence of a non-coordinated C=S bond. This enriched sample (M = Mo), displays two ^{13}C NMR resonances at 226.9 (s) and 292.3 ppm (quartet $^2J(CP) = 16$ Hz) due to the carbon atoms of two different CS_2 units, one of them therefore being C-bonded to the metal centre. The mode of bonding of the $M(CS_2)_2$ unit was determined by an X-ray study, which revealed that the two molecules of CS_2 have linked up to a head-to-tail carbon disulfide dimer, C_2S_4, which behaves as a trihapto four-electron donor ligand, as shown below.

As indicated above metallocyclic head-to-tail dimers of this type are often considered as intermediates in a number of heterocumulene disproportionations, although, as noted, this has never been conclusively demonstrated [27]. Furthermore, in the cases in which they have been isolated, they are stable, and do not rearrange, whereas when the disproportionation products are obtained no evidence for the formation of head-to-tail dimers has been found. Compounds XV exhibit high thermal stability, no traces of trithiocarbonate or thiocarbonyl compounds (i.e. of the disproportionation products) being found after they have heated at 120 °C for 3–4 h. An unexpected transformation, which yields CS_2 and the Mo^0 complex, $[Mo(S_2CPMe_3)(CO)_2(PMe_3)_2]$, takes place, however, upon reaction with CO (50 °C, 1 atm), as shown in eq. 7. This reaction corresponds to an oxidative, symmetric cleavage of the $C_2S_4{}^{2-}$ group, with formation of two molecules of CS_2; that is, the reverse of the metal-induced reductive dimerization (eq. 8).



(XV)



(XVI)

$$[Mo(C_2S_4)(C_2H_4)(PMe_3)_3] \xrightarrow{CO} [Mo(S_2CPMe_3)(CO)_2(PMe_3)_2] + CS_2 + \ldots \quad (7)$$

$$Mo^0 + 2CS_2 \rightarrow Mo^{II} + C_2S_4{}^{2-} \quad (8)$$

The yields of the Mo^0 complex and of CS_2 (isolated as CS_2PMe_3) become higher (ca. 50% vs. ca. 30%) when this reaction is carried out in the presence of added PMe_3. An attractive possibility for this reaction is to assume that the symmetric rupture of the C_2S_4 unit is induced by a nucleophilic attack of PMe_3 on the electrophilic molybdenum-bonded carbon atom of the C_2S_4 group, i.e., to consider compound XVI, previously characterized by Ibers and co-workers [32], as a model for the transition state or intermediate of this reaction.

Acknowledgment

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