Electron-rich metal complexes for CO_2 and CS_2 incorporation

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Abstract – The dihapto coordination of two molecules of carbon dioxide to
a square-planar MoP_2(P-P) fragment (P=monodentate-, P-P=bidentate phosphi-
ne ligands) can occur in several ways giving rise to different conformers.
Compounds of this type have been prepared and their spectroscopic proper-
ties investigated by variable temperature ^{1}H and ^{31}P NMR studies. The for-
mation of ethylene complexes related to $Mo(C_2H_4)_2(PMe_3)_4$, **6**, and the study
of their reactivity towards carbon dioxide and carbon disulphide is also
described. In particular, compound **6** induces a head-to-tail dimerization
of carbon disulphide with formation of a Mo(II)-C_2S_4 linkage, which, in
the presence of carbon monoxide, undergoes a symmetric, oxidative rupture,
which produces a Mo(0) complex and two molecules of carbon disulphide. The
insertion reactions of carbon dioxide and other unsaturated molecules into
the nickel-carbon bonds of the nickelacyclopentene complexes **9** have been
investigated and different organic products isolated by means of simple or
sequential insertion reactions.

INTRODUCTION

The reactions of carbon dioxide with transition metal complexes have been extensively inves-
tigated in the last decade. These investigations have led to the isolation of some stable
transition metal-carbon dioxide complexes, as well as to the observation of carbon-carbon
coupling reactions between carbon dioxide and a variety of organic substrates (refs. 1-5).
Considerable progress has been made in the understanding of the interaction of carbon dioxide
with transition metals but many important aspects of this chemistry remain little explored or
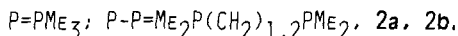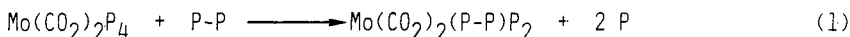underdeveloped, so that carbon dioxide chemistry is still a promising area of research.

In order to overcome the difficulties very often encountered in the study of the reactions of
carbon dioxide with transition metals, carbon disulphide and other related molecules (ref. 6)
have been used as models for carbon dioxide chemistry. However, the results obtained to date
clearly show that these molecules exhibit a very distinct chemical behaviour which only very
rarely parallels carbon dioxide chemistry. In particular, carbon disulphide displays a very
rich chemistry of much intrinsic academic interest. In this contribution we wish to report
some reactions of carbon dioxide with complexes of molybdenum and nickel, that lead to adduct
formation or to insertion into a metal-carbon bond. The reactions of these complexes with CS_2
are also described.

## CARBON DIOXIDE AND CARBON DISULPHIDE COMPLEXES OF MOLYBDENUM

Carbon dioxide complexes containing chelating phosphine ligands

Coordination of carbon dioxide in its intact form to a transition metal is a rare result and
the number of structurally characterized complexes is therefore very limited. At variance
with the behaviour found for other carbon dioxide complexes, the bis-carbon dioxide adduct
trans-$Mo(CO_2)_2(PMe_3)_4$, (**1**), has been reported to undergo a facile substitution of one of the
coordinated PMe_3 groups by an isocyanide ligand, with formation of trans,mer-$Mo(CO_2)_2(CNR)(P$
$Me_3)_3$ (ref. 7). Substitution of the carbon dioxide ligands is not observed, although at-
tempts to substitute a second phosphine by heating at 50-60°C, in the presence of an excess
of the isocyanide, lead to loss of carbon dioxide. We have now found (ref. 8) that chelating
diphosphine ligands effect substitution of two molecules of trimethylphosphine of complex **1**,
without change in the coordination mode of the carbon dioxide groups. Compounds, **2a-2b**, are
formed, as shown in reaction (1). The new complexes are yellow crystalline solids which dis-
play IR and NMR spectroscopic properties very similar to those reported for the parent com-
pound **1**. Our interest in complexes **2** was mainly concentrated in the following points:

i) assuming that the coordinated CO_2 ligands are staggered with respect to one another and

$$Mo(CO_2)_2P_4 \; + \; P\text{-}P \longrightarrow Mo(CO_2)_2(P\text{-}P)P_2 \; + \; 2\,P \qquad\qquad (1)$$

$$P=PMe_3; \; P\text{-}P=Me_2P(CH_2)_{1,2}PMe_2, \; \textbf{2a, 2b}.$$

eclipsing the P–Mo–P vectors of the equatorial plane, as predicted theoretically for **1** (ref. 9) and demonstrated by X-ray studies for the mono-isocyanide derivative (ref. 7), there could be three different conformations in compounds **2**, as represented in structures 3–5. Would any
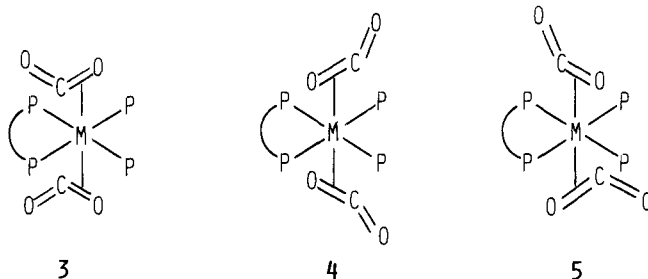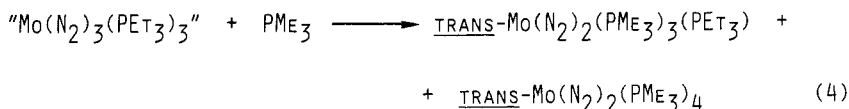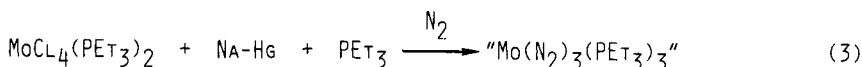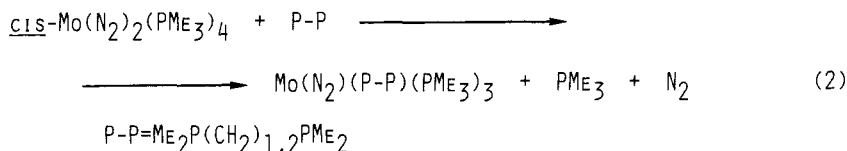

of these conformations be favoured in solution and in the solid state?.

ii) compounds **2**, as the parent complex **1**, are fluxional, and the process responsible for the observed changes in the NMR spectra is rotation around the molybdenum–carbon dioxide bond axis. Since there are two molecules of carbon dioxide coordinated to the molybdenum atom, the question arises as to what is the nature of the rotation process.

Variable temperature NMR studies provide some clues to both questions. The room temperature $^{31}P\{^1H\}$ NMR of complex **2a**, consists of two very broad and featureless humps, which give no useful information with regards to the structure of the compound. Upon cooling some changes are observed, and at –90°C four different sets of resonances (AMNX spin system) appear. This is in accord with structure 5 and not with 3 or 4. With respect to the second of the above questions, namely the nature of the fluxional process, a clear distinction between the possible mechanisms cannot be achieved with present data. In the low temperature limit (–75°C) the ^1H NMR spectrum of **2a** consists of two partially superimposed doublets for the PMe_3 ligands, as well as of four doublets, one for each of the dmpm methyl groups, in accord with the rigid structure 5 proposed for these complexes. Upon warming the spectrum simplifies and at 40°C it consists of one doublet for the trimethylphosphine groups and two doublets for the methyl protons of the chelating phosphine ligand, in agreement with a concerted, but not with a random rotation. Finally, in accord with these observations, the $^{31}P\{^1H\}$ NMR spectrum of compounds **2** consists, at high temperatures (60–80°C), of a pattern of lines characteristic of an AA'XX' spin system (ref. 8).
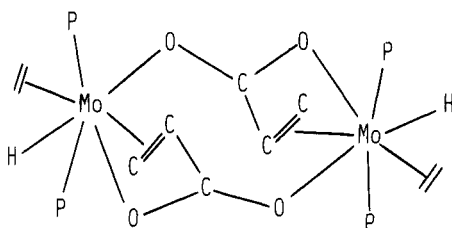
With the aim of obtaining new carbon dioxide complexes, the reactions of various dinitrogen complexes of molybdenum, prepared as summarized in reactions (2)–(4), with CO_2 have been stu-

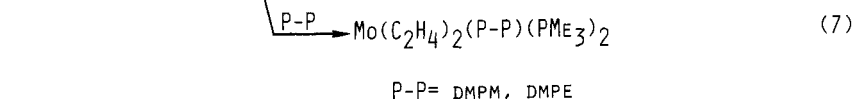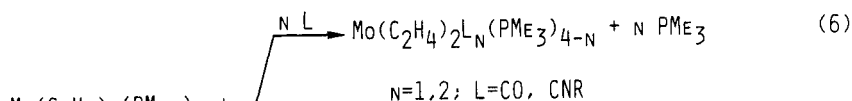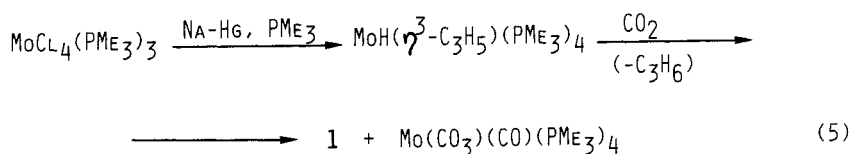$$\underline{cis}\text{-}Mo(N_2)_2(PMe_3)_4 \; + \; P\text{-}P \longrightarrow$$

$$\longrightarrow Mo(N_2)(P\text{-}P)(PMe_3)_3 \; + \; PMe_3 \; + \; N_2 \qquad (2)$$

$$P\text{-}P=Me_2P(CH_2)_{1,2}PMe_2$$

$$MoCl_4(PEt_3)_2 \; + \; Na\text{-}Hg \; + \; PEt_3 \xrightarrow{\;N_2\;} \text{''}Mo(N_2)_3(PEt_3)_3\text{''} \qquad (3)$$

$$\text{''}Mo(N_2)_3(PEt_3)_3\text{''} \; + \; PMe_3 \longrightarrow \underline{trans}\text{-}Mo(N_2)_2(PMe_3)_3(PEt_3) \; +$$

$$+ \; \underline{trans}\text{-}Mo(N_2)_2(PMe_3)_4 \qquad (4)$$

died. Reaction (3) produces in fact a mixture of the tris-dinitrogen complex and the dinitrogen bridged species $[Mo(N_2)_2(PEt_3)_2]_2(\mu\text{-}N_2)$, written in a simplified form as shown. Action of CO_2 upon solutions of these complexes provide only carbonate complexes, i. e., the products of the so-called reductive disproportionation of carbon dioxide, and therefore their investigation has not been pursued any further (ref. 10).

Reactions of *trans*-Mo(C₂H₄)₂(PMe₃)₄, (6), and related complexes with carbon dioxide and carbon disulphide

We have recently reported that carbon dioxide reacts with one of the coordinated ethylene ligands of complex **6**, forming a new C-C bond (ref. 11). The product of this reaction is a binuclear molybdenum complex which contains two bridging acrylate ligands (ref. 12), and the fa-

cile activation of carbon dioxide by complex **6** is probably a consequence of the electron-rich nature of the metal centre and of the availability of a vacant coordination position by facile dissociation of one of the trimethylphosphine ligands (ref. 11). In order to gain further information on this remarkable transformation other related systems have been investigated, reactions (5)-(7):

$$MoCl_4(PMe_3)_3 \xrightarrow{\text{Na-Hg, } PMe_3} MoH(\eta^3\text{-}C_3H_5)(PMe_3)_4 \xrightarrow[(-C_3H_6)]{CO_2}$$

$$\longrightarrow 1 + Mo(CO_3)(CO)(PMe_3)_4 \tag{5}$$

$$Mo(C_2H_4)_2(PMe_3)_4 + \begin{cases} \xrightarrow{N\ L} Mo(C_2H_4)_2L_N(PMe_3)_{4-N} + N\ PMe_3 & (6) \\ \quad N=1,2; \ L=CO, \ CNR \\ \xrightarrow{P-P} Mo(C_2H_4)_2(P-P)(PMe_3)_2 & (7) \end{cases}$$

$$P-P= \text{DMPM, DMPE}$$

i) attempts to prepare the propylene analogue of **6** lead instead to a hydrido allyl species (ref. 13) which reacts with carbon dioxide with evolution of propylene and formation of **1** and other products (ref. 10).

ii) PMe₃ substitution in **6** by the Π-acid ligands CO or CNR (ref. 14) affords new ethylene complexes as represented in reaction (6). Not unexpectedly, their reactivity towards carbon dioxide does not parallel that of **6**.
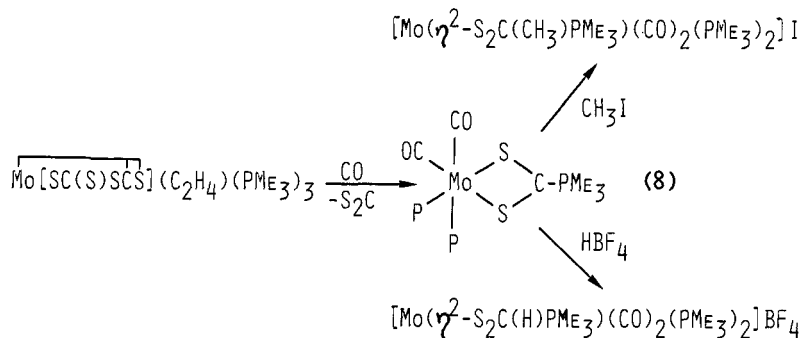
iii) compounds related to **6** containing chelating phosphine ligands can be prepared as depicted in equation (7). These compounds are surprisingly inert towards carbon dioxide. For instance, the dmpe derivative can be recovered unchanged after heating at 60°C, for several hours, in tetrahydrofuran, under 2-3 atm of carbon dioxide. The lack of reactivity in this case reflects probably the non availability of a vacant coordination position.

It was also of interest to ascertain if other heterocumulenes, in particular carbon disulphide, would undergo similar transformations. Addition of carbon disulphide to solutions of complex **6** produces a black solid of composition Mo(C_2S_4)(C_2H_4)(PMe₃)₃, (**7**), which has the PMe₃ groups in a meridional distribution. The ethylene ligand has equivalent CH₂ moieties but anysochronous methylenic protons, while the two CS₂ molecules give rise to a singlet and a quartet (^{13}C enriched sample of **7**, 227 and 293 ppm, respectively), suggesting that one of the carbon disulphide groups is C-bonded to the metal atom. The bonding mode of the C_2S_4 unit has been determined by X-ray studies (ref. 15) which show the two molecules of CS₂ have linked to a head-to-tail dimer. Formation of **7** can therefore be represented as in equation (8).

$$\text{TRANS-}Mo(C_2H_4)_2(PMe_3)_4 + 2CS_2 \longrightarrow \text{(structure)} + C_2H_4 + PMe_3 \tag{8}$$
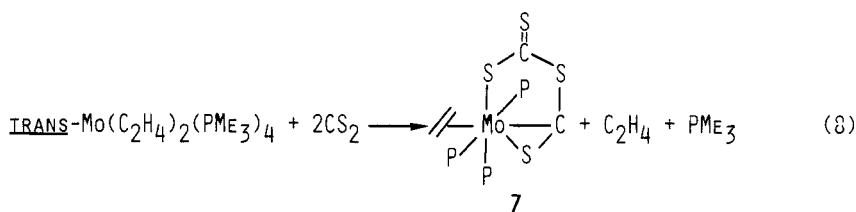
Metallocyclic complexes of this type are often proposed as intermediates in the metal-promoted reductive disproportionation of carbon dioxide and related molecules, although conclusive evidence has never been obtained (ref. 16). Furthermore, there is a surprising lack of studies aimed at the investigation of the chemical reactivity of these units. Compound **7** exhibits a high thermal stability and does not decompose, nor produces the disproportionation products, CS and CS_3^{2-}, after heating at 120°C for several hours. An unexpected reaction occurs with carbon monoxide under relatively mild conditions (50°C, 2 atm). As shown in Scheme I, symmetric oxidative rupture of the C_2S_4 unit is observed, with reduction to the molybdenum(0)

Scheme I

$$[Mo(\eta^2-S_2C(CH_3)PMe_3)(CO)_2(PMe_3)_2]I$$

$$Mo[SC(S)SCS](C_2H_4)(PMe_3)_3 \xrightarrow[-S_2C]{CO} \quad (8)$$

$$[Mo(\eta^2-S_2C(H)PMe_3)(CO)_2(PMe_3)_2]BF_4$$

complex **8**, i. e., the reverse of the reductive dimerization reaction. These results not only demonstrate a new type of reactivity for these metalacyclic units, but question their proposed intermediacy in the transition metal induced reductive disproportionation of heterocumulenes.

INSERTION CHEMISTRY OF THE NICKELACYCLOPENTENE COMPLEX $\overline{Ni[CH_2C(Me)_2\text{-}O\text{-}C_6H_4]}(PMe_3)_2$, 9a. REACTIONS WITH CARBON DIOXIDE, CARBON DISULPHIDE AND OTHER UNSATURATED MOLECULES

The nickelacyclopentene complex **9a** has a rich insertion chemistry and reacts with carbon monoxide, carbon dioxide, carbon disulphide and other unsaturated molecules (ref. 17) with formation of a variety of organic and metallo-organic products.
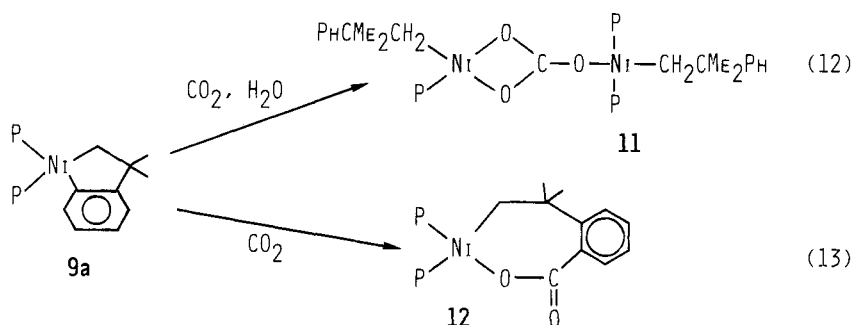
The interaction of **9a** with CO and PhC≡CPh, under ambient conditions, takes place as indicated in equations (9) and (10). As shown, insertion is followed by a rapid reductive elimination which yields the corresponding organic and metallo-organic products.

$$+ Ni(CO)_2(PMe_3)_2 \quad (9)$$
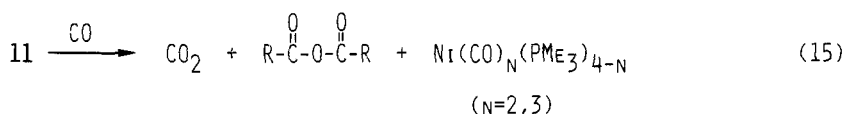

$$+ Ni(PhC\equiv CPh)(PMe_3)_2 \quad (10)$$
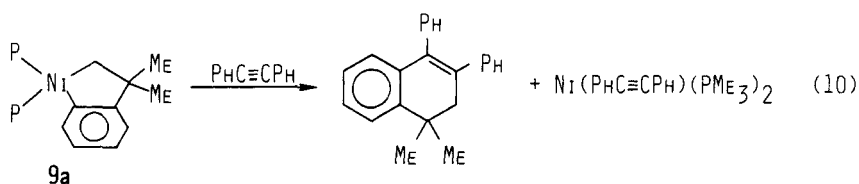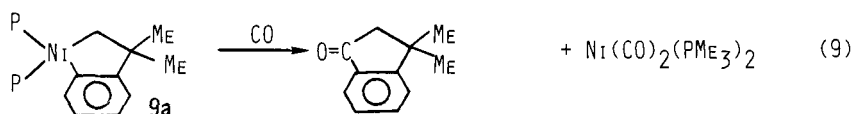
A differentiation between the two possible reaction pathways, namely insertion into the nickel-alkyl or aryl carbon bonds, can be accomplished by carrying out, in either order, the sequential insertions depicted in reaction (11) (ref. 18). Formation of **10** unequivocally stablishes that the insertion of CO takes place exclusively into the nickel-carbon alkyl bond.

$$\xrightarrow[\text{2. } CS_2 \text{ (OR CO)}]{\text{1. CO (OR } CS_2)} \quad (11)$$

10
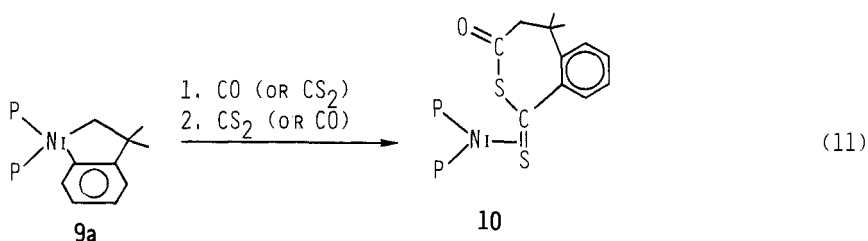
In the presence of wet CO_2, compound **9a** undergoes a fast protolytic cleavage of the nickel--aryl bond, with formation of the binuclear, carbonate-bridged species **11**, reaction (12). In the absence of water, the nickelalactone derivative **12** is formed as the result of the inser-
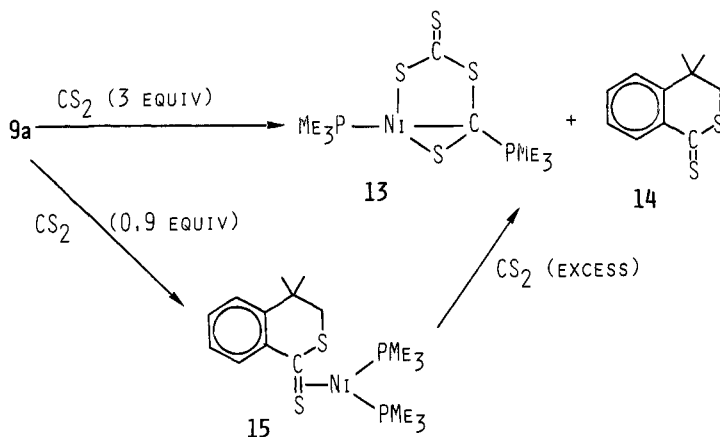
$$PHCME_2CH_2 \diagdown Ni \diagup O \diagdown C-O-Ni-CH_2CME_2PH \qquad (12)$$
$$\mathbf{11}$$

$$P \diagdown Ni \diagdown \qquad \xrightarrow{\;CO_2, \; H_2O\;}$$
$$\mathbf{9a}$$

$$\xrightarrow{\;CO_2\;} \qquad P \diagdown Ni \diagdown O-C=O \qquad (13)$$
$$\mathbf{12}$$

tion of carbon dioxide into the Ni–aryl bond (reaction 13). The existence in these compounds of Ni–C bonds, suggest further insertion chemistry can be pursued, and indeed, interaction with carbon monoxide (20°C, 1 atm) proceeds as indicated in reactions (14) and (15). While

$$\mathbf{12} \xrightarrow{\;CO\;} \quad O=C \cdots O-C=O \quad + \quad Ni(CO)_2(PME_3)_2 \qquad (14)$$

$$\mathbf{11} \xrightarrow{\;CO\;} \quad CO_2 \;+\; R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R \;+\; Ni(CO)_N(PME_3)_{4-N} \qquad (15)$$
$$(N=2,3)$$
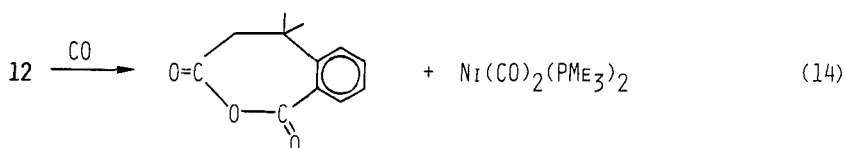
the former deserves no additional comments, the results of the latter reaction are rather unexpected, (ref. 17) since they correspond, in a formal sense, to a metal promoted oxidative conproportionation of carbonate and carbonyl ligands. Two molecules of carbon dioxide are formed, one of them is evolved as free CO_2 and the other becomes incorporated into the anhydride functionality.

The reaction of **9a** with 3-4 equiv of carbon disulphide (ref. 19) produces a red-brown microcrystalline precipitate of the known complex **13** (ref. 20), together with a red solution, from which red crystals of the dithiolactone **14** can be isolated (Scheme II). The nature of **13** and **14** implies the intermediacy of a Ni(0) species, **15**, which can, in fact, be isolated by the low temperature reaction of **9a** with a slight defect of carbon disulphide. As expected, **15** reacts with excess CS_2, with formation of **13** and **14**. It seems likely, that the first step in this reaction is insertion of carbon disulphide into the nickel–aryl carbon bond, and this has been confirmed, as already indicated, by isolation of complex **10**, as the result of the sequential insertion of carbon disulphide and carbon monoxide (see reaction 11). The resulting nickeladithiolactone intermediate species, which would in fact be the CS_2 analogue of **12**, undergoes reductive elimination, with concomitant intramolecular C–S bond formation, to yield the observed complex **15**.

Scheme II

$$\mathbf{9a} \xrightarrow{\;CS_2 \;(3\;EQUIV)\;} ME_3P-Ni \cdots C(PME_3) \quad + \quad \mathbf{14}$$
$$\mathbf{13}$$

$$\xrightarrow{\;CS_2\; (0.9\;EQUIV)\;} \mathbf{15} \xrightarrow{\;CS_2\;(EXCESS)\;}$$

A very different reaction is observed between carbon disulphide and complex **9b**, the dmpe
analogue of **9a**. Upon addition of 2 equiv of carbon disulphide to a solution of **9b**, the
trithiocarbonate **16** and the thioketene **17** are formed (Scheme III). This reaction corresponds
formally to a metal-induced reductive disproportionation of carbon disulphide but, rather
interestingly, it occurs without change in the oxidation state of the metal centre. Action of
1 equiv of carbon disulphide upon compound **9b** affords the 1,1-dithiolate species **18**, which,
as expected, reacts with another equivalent of carbon disulphide, with formation of **16** and **17**.
Thus, the course of the reaction of carbon disulphide with the nickelacyclopentene derivati-
ves **9** depends markedly on the nature of the phosphine co-ligands. It seems reasonable that
the reaction of **9b** with carbon disulphide proceeds also with initial insertion of the hetero-
cumulene into the nickel-aryl bond. The chelating nature of the dmpe ligand prevents phosphi-

Scheme III
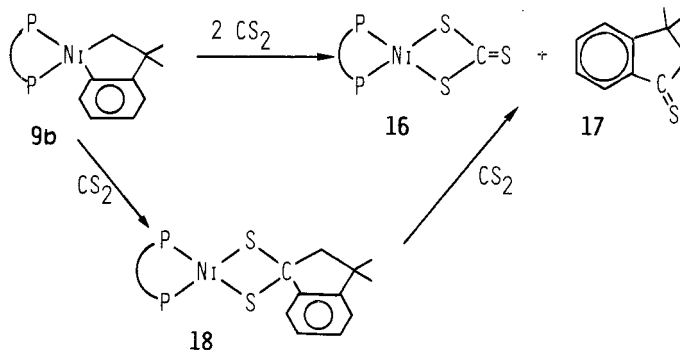
ne dissociation and may induce C-C instead of C-S bond formation. Nevertheless, electronic
factors must also play an important role and this is clearly manifested by the course of the
reaction of the 2,2'-bipyridine derivative **9c** (ref. 18) with carbon disulphide. As shown in
equation (16), this yields a complex containing the coordinated dithiolactone **14**, that is, a
product analogous to the trimethylphosphine derivative **15**. No evidence for the formation of a
1,1-dithiolate complex analogous to **18** has been found.
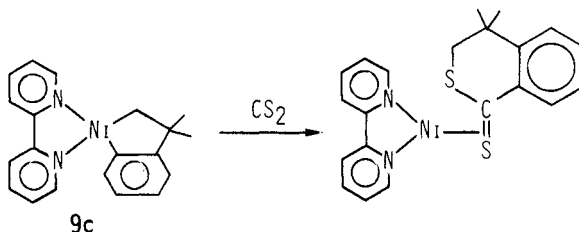
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