CENTENARY LECTURE*

Reactivities of Carbon Disulphide, Carbon Dioxide, and Carbonyl Sulphide Towards Some Transition-metal Systems

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1 Introduction

In this lecture I contrast the reactivities of the closely related molecules carbon disulphide, carbon dioxide, and carbonyl sulphide [CS_2, CO_2, and COS (connectivity OCS)] towards some low-valent transition-metal systems. The excitement here is that the chemistry of these closely related molecules is very diverse and often surprising and that this chemistry is not predictable from *a priori* theory but must be deduced experimentally. In addition there are some overtones of practical value. Carbon dioxide is potentially the most abundant source of C_1 chemistry, but ways must be found to activate the molecule catalytically if its potential is to be realized. Such activation is a matter of some urgency in this era of changing chemical feed stocks. Despite considerable research no catalytic reaction chemistry of a useful nature has been established for CO_2.[1] It is presumed, at least by transition-metal chemists, that such chemistry will be metal mediated. There is the implicit conviction, or perhaps the hope, that through the study of related molecules (*e.g.*, CS_2 and COS) on comparable transition-metal systems, some understanding of the reaction chemistry of these molecules and perhaps of CO_2 will be forthcoming.

In this lecture I will concentrate on a description of our own recent studies. I will first provide a brief glimpse at some CS_2 chemistry in order to illustrate the sensitivity of this chemistry to metal and ligand. I will then review the very sparse area of authentic, structurally characterized CO_2 complexes of transition metals and describe some of our recent experiments involving liquid CO_2. I will then provide some contrasts to these molecules through a discussion of some new results on the reactivity of COS towards these same transition-metal systems.

Table 1 provides a summary of some of the physical properties of CO_2, COS, and CS_2 to which we will refer in the ensuing discussion.

2 $M(PR_3)$ Complexes of CS_2 (M = Ni, Pd, or Pt)

The co-ordination chemistry of CS_2 has been extensively studied since the pre-

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*This is an expanded version of the Centenary Lecture first delivered at Queen's College, Belfast, on 27 April 1981.

[1] R. Eisenberg and D. E. Hendriksen, *Adv. Catal.*, 1979, **28**, 119.

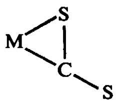
Table 1 *Selected physical properties of* CO_2, COS, *and* CS_2

Property	CO_2	COS	CS_2
b.p.	−78.5 °C	−50.2	46.3
ν	2349 cm^{-1}	2064	1530
	1342	859	658
	667	524	397
Δ(CO)*	126 kcal mol^{-1}	162	
Δ(CS)*		72	107
e.a.†	−0.6 eV	0.46	1.0

*The dissociation energy of the C—X bond [Δ(CX)] was estimated for the reaction XCY → X + CY under standard conditions. Thermochemical data were taken from 'JANAF Thermochemical Tables', ed. D. R. Stull and H. Prophet, U.S. Government Printing Office, Washington, D.C., 1971, 2nd Edn. and from D. L. Hildenbrand, *Chem. Phys. Lett.*, 1972, **15**, 379.

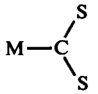
†Electron affinities as determined by R. N. Compton, P. W. Reinhardt, and C. D. Cooper, *J. Chem. Phys.*, 1975, **63**, 3821.

paration of the first transition-metal CS_2 complexes (M-CS_2) in 1967.[2] Carbon disulphide has proved to be a versatile ligand: it forms complexes with almost every transition metal; it shows a variety of insertion and disproportionation reactions;[3,4] it is believed to be capable of numerous modes of co-ordination to one or more metals, as deduced mainly from spectroscopic data. I emphasize the limitations of spectroscopic evidence, since the number of M-CS_2 structures, as deduced from diffraction methods, is surprisingly limited. For those complexes involving a single metal, only the η^2-co-ordination mode (1)* has been found.[5–11]


(1)

$M—S—C—S$

(2)


(3)

*In sketches of structures only connectivity is shown. There is no attempt to define bond orders.

[2] M. C. Baird and G. Wilkinson, *J. Chem. Soc. A*, 1967, 865.

[3] I. S. Butler and A. E. Fenster, *J. Organomet. Chem.*, 1974, **66**, 161.

[4] P. V. Yaneff, *Coord. Chem. Rev.*, 1977, **23**, 183.

[5] T. Kashiwagi, N. Yasuoka, T. Ueki, N. Kasai, M. Kakudo, S. Takahashi, and N. Hagihara, *Bull. Chem. Soc. Jpn.*, 1968, **41**, 296.

[6] R. Mason and A. I. M. Rae, *J. Chem. Soc. A*, 1970, 1767.

[7] M. G. B. Drew and L. S. Pu, *Acta Crystallogr., Sect. B*, 1977, **33**, 1207.

[8] H. Le Bozec, P. H. Dixneuf, A. J. Carty, and N. J. Taylor, *Inorg. Chem.*, 1978, **17**, 2568.

[9] H. Werner, K. Leonhard, and Ch. Burschka, *J. Organomet. Chem.*, 1978, **160**, 291.

[10] G. Fachinetti, C. Floriani, A. Chiesi-Villa, and C. Guastini, *Chem. Soc., Dalton Trans.*, 1979, 1612.

[11] G. Bianchini, C. Mealli, A. Meli, A. Orlandini, and L. Sacconi, *Inorg. Chem.*, 1980, **19**, 2968.

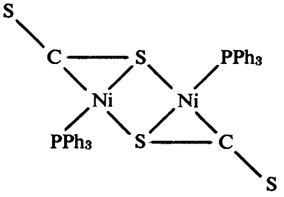
Modes (2)[12] and (3)[13] have been proposed from spectroscopic evidence. The range of structures proposed from spectroscopic data for M-CS_2 complexes in which more than one metal is involved is testimony to the fertile imagination of the co-ordination chemist. Only five crystal structures are known.[11,14–16]

The complexes Pt(η^2-CS_2)(PPh_3)$_2$ and Pd(η^2-CS_2)(PPh_3)$_2$, which were among the first M-CS_2 complexes to be prepared,[2] display co-ordination mode (1).[5,6] Our interest in such systems was generated by two observations: (i) the analogous complex Ni(CS_2)(PPh_3)$_2$ could not be synthesized;[2] (ii) the related CO_2 complex Ni(CO_2)(PCy_3)$_2$ is one of only three authentic M-CO_2 complexes, as deduced from diffraction methods (see Section 3 below). Thus we have explored the influence of the phosphine on the type of Ni-CS_2 complex formed and we summarize our results here.

The compounds of empirical formula Ni(CS_2)(PR_3) can be prepared by the reaction shown in equation (1).[17]

$$\mathrm{Ni(COD)_2 + PR_3 + CS_2 \rightarrow Ni(CS_2)(PR_3) + 2COD} \quad (\mathrm{R = Ph}, p\text{-tol, or Cy}) \quad (1)$$

The R = Ph compound was first prepared by a different route.[2] On the basis of the C—S stretching frequency of 1125 cm^{-1}, which is taken to indicate the presence of an unco-ordinated C—S linkage, the known propensity of Ni to be four co-ordinate, and the fact that the compound appeared to be dimeric in chloroform (though of very low solubility), it was assigned structure (4).[2] We find that the reaction shown in equation (1) yields complexes that have ratios for Ni:CS_2:PR_3 of 1:1:1, even if a 2:1 PR_3:Ni ratio of starting materials is used. Thus, we are also unable to prepare the Ni analogues of Pt(CS_2)(PR_3)$_2$. The R = Ph, *p*-tol, and Cy compounds of Ni have similar C—S stretching frequencies, 1122—1125 cm^{-1}, and colour (deep red) and so they are probably



(4)

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[12] H. Werner and W. Bertleff, *Chem. Ber.*, 1980, **113**, 267.

[13] J. E. Ellis, R. W. Fennell, and E. A. Flom, *Inorg. Chem.*, 1976, **15**, 2031.

[14] J. M. Lisy, E. D. Dobrzynski, R. J. Angelici, and J. Clardy, *J. Am. Chem. Soc.*, 1975, **97**, 656.

[15] T. G. Southern, U. Oehmichen, J. Y. Le Marouille, H. Le Bozec, D. Grandjean, and P. H. Dixneuf, *Inorg. Chem.*, 1980, **19**, 2976.

[16] T. S. Cameron, P. A. Gardner, and K. R. Grundy, *J. Organomet. Chem.*, 1981, **212**, C19.

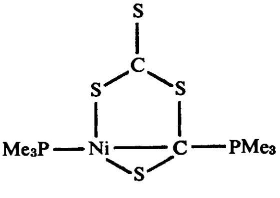
[17] M. G. Mason, P. N. Swepston, and J. A. Ibers, manuscript in preparation.

of similar structure. The R = Cy complex is even less soluble than the R = Ph complex, but the R = *p*-tol complex is modestly soluble in chlorinated hydrocarbon solvents and its $^{31}P\{^1H\}$ n.m.r. spectrum consists of a temperature invariant singlet at 21.2 ppm. Unfortunately, these solutions are sufficiently unstable so as to preclude determination of a molecular weight by cryoscopic means. Moreover, no single crystals of these materials have been obtained. We are thus left with an unsatisfactory characterization. The evidence does not eliminate (4), but it is consistent also with other structures, especially if the complexes are other than dimers.

Products of a different stoicheiometry are formed in the following reaction:[17]

$$\text{Ni(COD)}_2 + 2\text{PR}_3 + 2\text{CS}_2 \rightarrow \text{`Ni(CS}_2)_2(\text{PR}_3)_2\text{'} + 2\text{COD} \qquad (2)$$
$$(\text{R = Me or Et})$$

The stoicheiometry of the product is independent of the ratios of starting materials. These compounds have proven impossible to characterize spectroscopically, although their general stability has provided more opportunity for study. On the basis of $^{31}P\{^1H\}$, ^1H, and ^{13}C n.m.r. data, the last from an enriched sample, and on the basis of the low C—S stretching frequencies of 1010 and 850 cm^{-1} we deduced that one PR_3 group is bound to Ni, one CS_2 group is bound to Ni, but that the other PR_3 and CS_2 molecules are bound to one another. Several examples of the phosphoniodithiocarboxylato ligand (R_3PCS_2) are known.[12,18–22] The cryoscopic molecular weights of these compounds indicate that they are monomers and the persistence of the solid state structure in solution was verified by solution infrared spectra. Although these physical and spectroscopic data enabled us to eliminate many possible structures, we were unable to deduce a unique structure. Single crystals of the R = Me complex were obtained and the compound is actually (5).[17] The existence of a '$C_2S_4PR_3$' ligand is unprecedented. Previous examples of phosphoniodithiocarboxylato linkages



(5)

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[18] P. W. Armit, W. J. Sime, T. A. Stephenson, and L. Scott, *J. Organomet. Chem.*, 1978, **161**, 391.

[19] S. M. Boniface and G. R. Clark, *J. Organomet. Chem.*, 1980, **188**, 263.

[20] P. K. Baker, K. Broadley, and N. G. Connelly, *J. Chem. Soc., Chem. Commun.*, 1980, 775.

[21] C. Bianchini, A. Meli, A. Orlandini, and G. Scapacci, *J. Organomet. Chem.*, 1981, **215**, C59.

[22] T. R. Gaffney and J. A. Ibers, *Inorg. Chem.*, in the press.

have involved co-ordination of both sulphur atoms to the metal atom. Coupling of two CS_2 molecules about transition metals has been seen previously,[23,24] but these complexes lack the presence of a phosphine molecule on the C_2S_4 fragment.

This example illustrates a familiar but often forgotten fact. Even with extensive spectroscopic data, in the present instance including n.m.r. spectra of three different nuclei within the molecule, the unequivocal characterization of a new compound with unprecedented connectivity is usually not possible. Spectroscopic data provide a rapid and generally reliable means of characterization if there is a structural base built on the results from diffraction studies.

From this brief summary it is clear that the nature of the Ni-CS_2 compound formed is critically dependent upon the phosphine. In no instance is the resultant Ni-CS_2 complex the direct analogue of the compounds formed with Pt or Pd and PPh_3. When we examine the nature of the products formed between CO_2 or COS and the phosphines of the Ni triad we will again see this manifestation of the subtle balance of electronic and steric forces.

3 Reactivity of CO_2

In contrast to CS_2, CO_2 is somewhat unreactive towards transition-metal systems.[1] In particular, its co-ordination chemistry is very sparse. Eisenberg and Hendriksen[1] recently reviewed the co-ordination chemistry of carbon dioxide and summarized some examples of metal complexes originally believed to be those of carbon dioxide that on further examination turned out to be otherwise. Because of difficulties of spectroscopic characterization, the unpredictable effects of adventitious water, and the tendency of co-ordinated CO_2 to react further, it is prudent to accept structural characterization by diffraction methods as the criterion by which to judge the authenticity of a given class of transition-metal–carbon dioxide complexes (M-CO_2). To our knowledge only three M-CO_2 complexes, $Ni(\eta^2\text{-}CO_2)(PCy_3)_2$,[25] $K[Co(Pr\text{-}salen)(\eta^1\text{-}CO_2)]$,[26] and $Nb(\eta^5\text{-}C_5H_4Me)_2(CH_2SiMe_3)(\eta^2\text{-}CO_2)$[27] have been characterized, despite the intense effort that has been devoted to the preparation of such complexes. The Ni complex appears to have the correct balance of electronic and steric factors for the stabilization of bound CO_2, as the complexes $M(\eta^2\text{-}CO_2)(PR_3)_2$ [M = Pd or Pt; R = Cy (*vide infra*) or Ph[28]] cannot be prepared. Recall the varied chemistry of M-CS_2 phosphine complexes of the Ni triad. The stability of the Nb complex has been ascribed to its co-ordinative saturation and to the fact that the orientation of the bound CO_2 ligand disfavours an internal decomposition route. The stability of the Co complex has been ascribed to the simultaneous

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[23] M. Cowie and S. K. Dwight, *J. Organomet. Chem.*, 1980, **198**, C20.

[24] H. Werner, O. Kolb, R. Feser, and U. Schubert, *J. Organomet. Chem.*, 1980, **191**, 283.

[25] M. Aresta, C. F. Nobile, V. G. Albano, E. Forni, and M. Manassero, *J. Chem. Soc., Chem Commun.* 1975, 636.

[26] G. Fachinetti, C. Floriani, and P. F. Zanazzi, *J. Am. Chem. Soc.*, 1978, **100**, 7405.

[27] G. S. Bristow, P. B. Hitchcock, and M. F. Lappert, *J. Chem. Soc., Chem Commun.*, 1981, 1145.

[28] C. J. Nyman, C. E. Wymore, and G. Wilkinson, *J. Chem. Soc. A*, 1968, 561.

involvement of the Lewis acid site at C with Co and of the Lewis base site at O with K.

The existence of these three M-CO_2 complexes provides meagre clues as to how one might develop a general co-ordination chemistry of CO_2. What is needed at this stage is a convenient method of surveying the reactivity of CO_2 towards a wide spectrum of transition-metal complexes. Whereas previous studies have used gaseous CO_2, we have carried out some experiments on the reactivity of a number of transition-metal complexes towards *liquid* CO_2.[29] The benefits of using liquid CO_2 are a greatly increased CO_2 concentration and the elimination of solvent competition for a vacant co-ordination site on the metal. Therefore, the use of liquid CO_2 may be an effective way to survey metal complexes for their ability to bind CO_2. The metal systems we have examined to date generally have the following characteristics: a low-valent metal atom is surrounded by electron donating ligands, usually trialkylphosphine ligands; the compound is either co-ordinatively unsaturated or contains an easily displaceable ligand, such as N_2 or an olefin; at least some of the ligands about the metal are sterically demanding.

Some claims of the synthesis of M-CO_2 complexes have been vitiated by subsequent discovery of adventitious water in the reactions. Although liquid CO_2 can be dried reasonably effectively over molecular sieves, we have taken the following conservative approach. If, on the basis of spectroscopic examination of the products, a reaction of the transition-metal system with liquid CO_2 was judged to have occurred, the experiment was repeated with water deliberately added to the reaction mixture. If the yield of the same product increased, then the reaction was assumed to require wet CO_2; if the yield of product did not change, the reaction was assumed to occur with dry CO_2.

We divide our findings on the reactivity of transition-metal complexes towards liquid CO_2 into three categories: no reaction; reaction with dry CO_2; reaction with wet CO_2. The various reactivities are summarized in Table 2.

A. No Reaction.—As Table 2 indicates, a number of the complexes studied show no reactivity towards liquid CO_2. These compounds were recovered unchanged from the reaction vessel. Yet the conditions were certainly forcing, with no solvent present and with a CO_2:M ratio of perhaps 1000:1. Although we did not probe the reaction mixtures under pressure (70 atm at 25 °C), at least for the N_2-containing complexes of Table 2 the persistence of N_2 as a ligand argues against CO_2 reactivity at high pressure. Thus CO_2 did not displace N_2 from $IrCl(N_2)(PPh_3)_2$. There is no evidence that CO_2 will insert into the Ir—R bond of $IrR(CO)(PPh_3)_2$, (R = Me or Ph).

Although $[Ni(PCy_3)_2]_2(\mu\text{-}N_2)$ is known[30] to react with CO_2(g) to afford $Ni(\eta^2\text{-}CO_2)(PCy_3)_2$,[25] and indeed this same complex is formed with CO_2(l) (*vide infra*), the closely related complexes $Pd(PCy_3)_2$ and $Pt(PCy_3)_2$ do not react

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[29] M. G. Mason and J. A. Ibers, *J. Am. Chem. Soc.*, in the press.

[30] P. W. Jolly, K. Jonas, C. Krüger, and Y.-H. Tsay. *J. Organomet. Chem.*, 1971, 33, 109.

Table 2 *Reactivity of some transition-metal systems towards liquid* CO_2

Complex	*Reacts with dry* CO_2	*Reacts with wet* CO_2
$IrCl(N_2)(PPh_3)_2$	No	
$IrR(CO)(PPh_3)_2$ (R = Me or Ph)	No	
$IrR(O_2)(CO)(PPh_3)_2$ (R = Me or Ph)	Yes	
$[RhH(PCy_3)_2]_2(\mu\text{-}N_2)$	No	
$[Ni(PCy_3)_2]_2(\mu\text{-}N_2)$	Yes	
$Pd(PCy_3)_2$	No	
$Pt(PCy_3)_2$	No	Yes
$Mo(CO)_3(PCy_3)_2$	No	
$W(CO)_3(PCy_3)_2$	No	Yes
$[Co(PPh_3)_3]_2(\mu\text{-}N_2)$	No	
$[Co(PEt_2Ph)_3]_2(\mu\text{-}N_2)$	Yes	
$Na[Co(N_2)(PEt_2Ph)_3]$	Yes	

with dry CO_2, although the Pt compound does react with wet CO_2. Nor does the related Rh system, $[RhH(PCy_3)_2]_2(\mu\text{-}N_2)$ display any reactivity towards CO_2. Finally, the earlier transition-metal systems, $M(CO)_3(PCy_3)_2$ (M = Mo or W), do not react with dry CO_2, although the W complex does react with wet CO_2. The reaction chemistry of $W(CO)_3(PCy_3)_2$ is very rich.[31] Reactions occur with CO, H_2, SO_2, C_2H_4, and N_2. The lack of reactivity of the complex towards CO_2 again emphasizes the formidable problems in activating CO_2.

B. Reactions with Dry CO_2.—The compounds $IrR(O_2)(CO)(PPh_3)_2$ show reactivity towards dry CO_2(l). On the basis of infrared and n.m.r. evidence we believe that the products are the peroxycarbonates $IrR(OCO_3)(CO)(PPh_3)_2$. An analogous reaction is known between $Pt(O_2)(PCy_3)_2$ and CO_2.[32]

The formation of $IrR(OCO_3)(CO)(PPh_3)_2$ from $IrR(O_2)(CO)(PPh_3)_2$ is probably an example of external attack by CO_2 on a co-ordinated species. The compounds $IrR(O_2)(CO)(PPh_3)_2$ are co-ordinately saturated, and even if an open co-ordination site were provided by PPh_3 dissociation, CO_2 co-ordination to the iridium atom would seem unlikely because of the demonstrated inertness of $IrCl(N_2)(PPh_3)_2$ and $IrR(CO)(PPh_3)_2$ to CO_2. Kinetic measurements[33] for the reaction of hexafluoroacetone with $IrCl(O_2)(CO)(PPh_3)_2$ to form $IrCl[O_2C(CF_3)_2O](CO)(PPh_3)_2$ are consistent with a similar external attack mechanism for this reaction.

The ready displacement of the N_2 ligand from $[Ni(PCy_3)_2]_2(\mu\text{-}N_2)$[30] led us to examine other first-row transition-metal dinitrogen complexes. The compound $[Co(PEt_2Ph)_3]_2(\mu\text{-}N_2)$ reacts with liquid CO_2 to yield a highly air-sensitive red oil. The reaction is accompanied by the release of PEt_2Ph. There is spectroscopic

[31] G. J. Kubas, *J. Chem. Soc., Chem. Commun.*, 1980, 61.
[32] Y. Tatsuno and S. Otsuka, *J. Am. Chem. Soc.*, 1981, **103**, 5832.
[33] W. B. Beaulieu, G. D. Mercer, and D. M. Roundhill, *J. Am. Chem. Soc.*, 1978, **100**, 1147.

evidence for CO and CO_3^{2-} in the product. The reductive disproportionation of CO_2 to CO and CO_3^{2-} has been observed previously in $[Mo(CO_3)(CO)(PMe_2Ph)_3]_2$,[34] $[Ti(C_5H_5)_2]_4(CO_3)_2$,[35] and the reaction of $Na[Fe(C_5H_5)(CO)_2]$[36] with CO_2. The intermediacy of a C_2O_4 ligand, as observed in $IrCl(C_2O_4)(PMe_3)_3$,[37] is an attractive idea, but has not been conclusively demonstrated for any system to date. Similar chemistry was seen for $Na[Co(N_2)(PEt_2Ph)_3]$ in liquid CO_2. In these instances intermediate CO_2 complexes were probably formed. Such complexes, not stabilized by steric bulk, are open to attack by additional CO_2, ultimately leading to reductive disproportionation to CO and CO_3^-. The use of steric bulk to stabilize highly reactive CO_2 complexes is clearly important. That $[Co(PPh_3)_3]_2(\mu\text{-}N_2)$ is inert to $CO_2(l)$ whereas the analogous PEt_2Ph complex is not emphasizes the importance of electronic factors in CO_2 reactivity. Presumably the lower basicity of PPh_3, compared with PEt_2Ph, prevents CO_2 co-ordination to the Co centre.

The reaction of $[Ni(PCy_3)_2]_2(\mu\text{-}N_2)$ with $CO_2(g)$ was first reported to afford $[Ni(PCy_3)_2]_2(\mu\text{-}CO_2)$.[30] Later $Ni(\eta^2\text{-}CO_2)(PCy_3)_2$ was isolated from this reaction, as characterized by a single crystal *X*-ray diffraction study.[25] We find that this complex may be prepared in high yield in liquid CO_2.

C. Reactions with Wet CO_2.—We find that $W(CO)_3(PCy_3)_2$ reacts both with H_2O and with CO_2–H_2O mixtures. As deduced spectroscopically the product with H_2O is the complex $WH(OH)(CO)_3(PCy_3)_2$, a member of a small class of hydrido–hydroxo complexes formed by oxidative addition of H_2O to transition-metal systems.[38–41] Reaction of $WH(OH)(CO)_3(PCy_3)_2$ in liquid CO_2 produces $WH(O_2COH)(CO)_3(PCy_3)_2$, a labile bicarbonato complex, which *in vacuo* reverts to $W(CO)_3(PCy_3)_2$. The product probably results from external attack of the CO_2 molecule on the W—OH linkage, as it seems unlikely that CO_2 could co-ordinate to a seven-co-ordinate W atom prior to insertion.

The compound $Pt(PCy_3)_2$, which is known to react with H_2O,[40] reacts with wet CO_2 to produce what we believe to be *trans*-$PtH(O_2COH)(PCy_3)_2$. Two closely related compounds, *trans*-$PtH(\eta^1\text{-}O_2COMe)(PCy_3)_2$[42] and *trans*-$Pd(Me)(\eta^1\text{-}O_2COH)(PEt_3)_2$,[43] are known. The formation of *trans*-$PtH(O_2COH)(PCy_3)_2$ from the reaction of $Pt(PCy_3)_2$ with wet $CO_2(l)$ could proceed through CO_2

[34] J. Chatt, M. Kubota, G. J. Leigh, F. C. March, R. Mason, and D. J. Yarrow, *J. Chem Soc., Chem. Commun.*, 1974, 1033.

[35] G. Fachinetti, C. Floriani, A. Chiesi-Villa, and C. Guastini, *J. Am. Chem. Soc.*, 1979, **101**, 1767.

[36] G. O. Evans, W. F. Walter, D. R. Mills, and C. A. Streit, *J. Organomet. Chem.*, 1978, **144**, C34.

[37] T. Herskovitz and L. J. Guggenberger, *J. Am. Chem. Soc.*, 1976, **98**, 1615.

[38] R. D. Gillard, B. T. Heaton, and D. H. Vaughan, *J. Chem. Soc. A*, 1970, 3126.

[39] C. R. Eady, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1977, 838.

[40] T. Yoshida, T. Matsuda, T. Okano, T. Kitani, and S. Otsuka, *J. Am. Chem. Soc.*, 1979, **101**, 2027.

[41] T. Yoshida, T. Okano, K. Saito, and S. Otsuka, *Inorg. Chim. Acta*, 1980, **44**, L135.

[42] A. Immirzi and A. Musco, *Inorg. Chim. Acta*, 1977, **22**, L35.

[43] R. J. Crutchley, J. Powell, R. Faggiani, and C. J. L. Lock, *Inorg. Chim. Acta*, 1977, **24**, L15.

attack on a *trans*-$PtH(OH)(PCy_3)_2$ intermediate, formed by oxidative addition of H_2O to $Pt(PCy_3)_2$, or by oxidative addition of H_2CO_3 to $Pt(PCy_3)_2$.

The results here for the Ni triad provide a dramatic illustration of the importance of electronic factors in CO_2 co-ordination. The compound $[Ni(PCy_3)_2]_2(\mu\text{-}N_2)$, which in solution is in equilibrium with $Ni(N_2)(PCy_3)_2$, readily forms with $CO_2(g)$[30] or $CO_2(l)$ the modestly stable compound $Ni(\eta^2\text{-}CO_2)(PCy_3)_2$.[25] It does not matter whether the CO_2 is dry or wet. The analogous Pd complex, $Pd(PCy_3)_2$, is unreactive towards either dry or wet $CO_2(l)$. Finally the complex $Pt(PCy_3)_2$, although unreactive towards dry $CO_2(l)$, reacts with wet $CO_2(l)$ to afford *trans*-$PtH(O_2COH)(PCy_3)_2$.

The use of liquid CO_2 provides a means for convenient and rapid screening of the reactivity of various transition-metal systems towards CO_2. From the brief summary presented it is clear that there is a considerable body of insertion chemistry, although CO_2 appears to form far fewer stable metal complexes than does CS_2. To contrast further the chemistry of CO_2 and CS_2 we now turn to the reactivity of the intermediate molecule, COS.

4 Reactivity of COS

About three years ago we turned to the study of the reactivity of COS towards transition metals, since little was known about COS reactions and the intermediacy of COS between CS_2 and CO_2 intrigued us. A brief account of some of this work has appeared.[44]

In 1967 the first M-COS complex, $Pt(COS)(PPh_3)_2$, was reported.[2] Subsequently, a few other M-COS complexes were prepared.[45,46] We therefore anticipated that M-COS complexes would be easy to prepare and through an investigation of the mode of co-ordination of the COS molecule we would obtain some clues as to the factors that stabilize the various modes and possibly the bonding of CO_2. We are now wiser: COS complexes are the exception rather than the rule, and COS shows some very interesting and versatile chemistry. In addition to COS co-ordination, carbonylation reactions and abstraction of sulphur are common. Here we discuss briefly these various reactions, providing where we can comparisons with the analogous CS_2 reactions. If reactions with CO_2 are not mentioned it may be assumed that they do not occur.

Carbon disulphide reacts with $Fe(CO)_2(PPh_3)_3$ to give $Fe(CO)_2(\eta^2\text{-}CS_2)(PPh_3)_2$ and PPh_3, as shown in equation (3).

$$Fe(CO)_2(PPh_3)_3 + CS_2 \rightarrow Fe(CO)_2(\eta^2\text{-}CS_2)(PPh_3)_2 + PPh_3 \qquad (3)$$

In contrast, COS carbonylates $Fe(CO)_2(PPh_3)_3$ in toluene according to equation (4).[47]

$$Fe(CO)_2(PPh_3)_3 + COS \rightarrow Fe(CO)_2(PPh_3)_3 + SPPh_3 \qquad (4)$$

If the reaction is performed in liquefied COS, $Fe(S_2CO)(CO)_2(PPh_3)_2$ is also formed.

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[44] J. A. Ibers, T. R. Gaffney, and K. D. Schramm, *IUPAC Coord. Chem.*-21, 1981, 141.

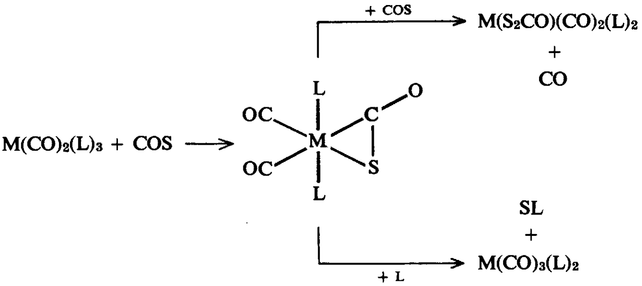
[45] H. L. M. van Gaal and J. P. J. Verlaan, *J. Organomet. Chem.*, 1977, **133**, 93.

[46] E. Uhlig and W. Poppitz, *Z. Chem.*, 1979, **19**, 191.

[47] T. R. Gaffney and J. A. Ibers, *Inorg. Chem.*, in the press.

$$Fe(CO)_2(PPh_3)_3 + COS(l) \rightarrow Fe(S_2CO)(CO)_2(PPh_3)_2 + Fe(CO)_3(PPh_3)_2 + SPPh_3 \quad (5)$$

These results are consistent with the initial formation of $Fe(\eta^2\text{-}COS)(CO)_2(PPh_3)_2$ as an unstable intermediate, which rapidly decomposes in toluene and reacts with COS in liquefied COS, as shown in Scheme 1.



Scheme 1

We have isolated $Ru(CO)_2(\eta^2\text{-}COS)(PPh_3)_2$ [equation (6)][47] and have shown that it reacts with COS and PPh_3 in accordance with Scheme 1. The complex is stable in the solid state when stored under an atmosphere of nitrogen, but it is unstable in solution.

$$Ru(CO)_2(PPh_3)_3 + COS \rightarrow Ru(CO)_2(\eta^2\text{-}COS)(PPh_3)_2 + PPh_3 \quad (6)$$

The carbon disulphide analogues of $Ru(CO)_2(\eta^2\text{-}COS)(PPh_3)_2$ and $Fe(CO)_2(\eta^2\text{-}COS)(PPh_3)_2$ have been prepared [48,49] and are much more stable than the COS complexes. Since vigorous conditions are often required, sulphur abstraction from a $M\text{-}(\eta^2\text{-}CS_2)$ complex[50] is not a general method for the preparation of metal-thiocarbonyls. In contrast, sulphur elimination from $M\text{-}(\eta^2\text{-}COS)$ complexes is much more facile. Metal complexes that form stable CS_2 complexes often react with COS to give a carbonylation product.[45,46,51]

Another isolable COS complex is, of course, $Pt(\eta^2\text{-}COS)(PPh_3)_2$, the first reported M-COS complex.[2] It is readily formed by the reaction of COS with a hexane suspension of $Pt(PPh_3)_3$. The $^{31}P\{^1H\}$ n.m.r. spectrum of $Pt(\eta^2\text{-}COS)(PPh_3)_2$ is consistent with the proposed structure and the J and δ values are very similar to those of $Pt(\eta^2\text{-}CS_2)(PPh_3)_2$; thus the environments of the P nuclei in the two complexes are similar. Although the mode of attachment of COS and CS_2 to the $Pt(L)_2$ metal centre is the same, the strength of the C—S bond is not, as evidenced by the reactivity of the COS complex (*vide infra*) and the stability of the CS_2 complex. The $^{31}P\{^1H\}$ n.m.r. spectrum of $Pt(\eta^2\text{-}COS)(PPh_3)_2$ is

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[48] M. C. Baird, G. Hartwell, Jr., and G. Wilkinson, *J. Chem Soc. A*, 1967, 2037.

[49] K. R. Grundy, R. O. Harris, and W. R. Roper, *J. Organomet. Chem.*, 1975, **90**, C34.

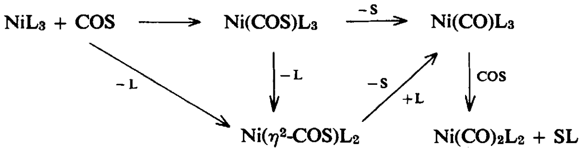
[50] I. S. Butler, *Acc. Chem. Res.*, 1977, **10**, 359 and references therein.

[51] H. Werner, S. Lotz, and B. Heiser, *J. Organomet. Chem.*, 1981, **209**, 197.

invariant to temperature up to the point where decomposition becomes significant (−20 °C), and thus no fluctional processes of the COS ligand occur on the n.m.r. time scale.[52] Similarly, the CS_2 complex is rigid on the n.m.r. time scale,[53] whereas $Ni(\eta^2\text{-}CO_2)(PCy_3)_2$ is fluctional above −50 °C.[29] The ability of olefins to accept electron density from NiL_3 complexes has been correlated with the strength of the bonding interaction.[54] The electron affinities of CS_2, COS, and CO_2 (Table 1) correlate well with the observed reactivities of these ligands towards basic metal complexes, and the fluctional behaviour of the CO_2 complex is probably a reflection of the weaker back donation to the C—O bound ligand.

Similarly, the reaction of $Pd(PPh_3)_3$ or $Pd(PPh_3)_4$ with COS results in the formation of $Pd(\eta^2\text{-}COS)(PPh_3)_2$;[52] however, the product is very unstable. With $P(p\text{-tol})_3$, a slightly more basic phosphine, a more stable product is obtained.

In contrast, the reaction of $Ni(PPh_3)_3$ with COS results in stepwise carbonylation,[52] as shown in Scheme 2. Formation of $Ni(CO)(PPh_3)_3$ could proceed through formation of $Ni(COS)(PPh_3)_3$ as an intermediate, which could then eliminate sulphur to give $Ni(CO)(PPh_3)_3$ or PPh_3 to afford $Ni(\eta^2\text{-}COS)(PPh_3)_2$. A similar mechanism has been proposed for the formation of $Ni(\eta^2\text{-}CO_2)(L)_2$ [L = PEt_3, $P(n\text{-}Bu)_3$][55] and the presence of $Ni(CO_2)(L)_3$ has been detected spectroscopically. The complex $Ni(\eta^2\text{-}CO_2)(L)_2$ is stable, whereas similar reactions with COS afford a mixture of metal carbonyls.[46]



Scheme 2

The stability of the species $M(\eta^2\text{-}COS)(L)_2$ (L = PPh_3) decreases in the order Pt > Pd > Ni. The platinum complex is stable in solution at low temperature, the palladium complex is stable in the solid state but decomposes upon dissolution, and the nickel complex has not been observed, although it is likely to be a transient intermediate in the observed carbonylation reaction. Contrast this stability order with that of $M(\eta^2\text{-}CO_2)(PCy_3)_2$ (Section 3). The reactions of ML_3 complexes with COS depend on the affinity of the metal centre for carbon monoxide and sulphur, the species into which COS fragments upon C—S bond cleavage. Palladium and platinum have a higher affinity for sulphur than does nickel, and the formation of dithiocarbonates is favoured (*vide infra*). Nickel(0) complexes have a high affinity for π-acceptor ligands [*e.g.*, $Ni(CO)_4$ is stable, $Pt(CO)_4$ is not], and $Ni(PPh_3)_3$ selectively binds the CO fragment.

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[52] T. R. Gaffney and J. A. Ibers, *Inorg. Chem*, in the press.

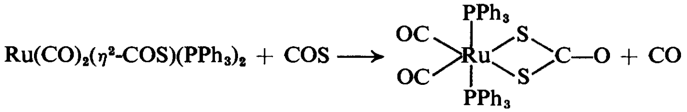
[53] P. J. Vergamini and P. G. Eller, *Inorg. Chim. Acta*, 1979, **34**, L291.

[54] C. A. Tolman, *J. Am. Chem. Soc.*, 1974, **96**, 2780.

[55] M. Aresta and C. F. Nobile, *J. Chem. Soc., Dalton Trans.*, 1977, 708.

It is interesting that $Pt_2S(CO)(PPh_3)_3$ reacts with CS_2 to afford $Pt(CS_3)(PPh_3)_2$,[56] but addition of CS_2 to $Pt(PPh_3)_4$ affords $Pt(\eta^2\text{-}CS_2)(PPh_3)_2$.[2] This complex is stable, and C—S bond cleavage to give $Pt_2S(CS)(PPh_3)_3$ does not occur. Hence, it is the greater stability of the co-ordinated C—S bond of CS_2 that prevents the formation of $Pt(CS_3)(PPh_3)_2$ from $Pt(PPh_3)_4$ and CS_2 by a pathway analogous to Scheme 2.

Carbonyl sulphide affords a convenient route to metal dithiocarbonates. Thus COS reacts with $Ru(CO)_2(\eta^2\text{-}COS)(PPh_3)_2$ to afford $Ru(S_2CO)(CO)_2(PPh_3)_2$, as shown in equation (7).[52] Although addition of excess COS to



(7)

$Pt(PPh_3)_3$ in acetone has been reported to yield a bis(carbonyl sulphide) complex, $Pt(COS)_2(PPh_3)_2$,[57] we[52] find that $Pt(PPh_3)_3$ or $Pt(PPh_3)_4$ reacts with excess COS to afford a dithiocarbonate:

$$Pt(PPh_3)_4 + \text{excess } COS \rightarrow Pt(COS_2)(PPh_3)_2 \qquad (8)$$

The similarity of the analytical and spectroscopic data to those reported for '$Pt(COS)_2(PPh_3)_2$' leads us to suggest that this complex be reformulated as $Pt(COS_2)(PPh_3)_2$.

These reactions that result in the formation of dithiocarbonates represent a two-electron oxidation of the metal and disproportionation of two molecules of COS. It was recently reported[58] that vanadocene promotes this two-electron disproportionation of COS. A C—O bound carbonyl sulphide complex is proposed, and nucleophilic attack by the exocyclic sulphur atom upon the electrophilic carbon atom of another molecule of COS leads to formation of the products, a metal dithiocarbonate and a metal carbonyl. For a C—S bound carbonyl sulphide, nucleophilic attack by the exocyclic oxygen atom would lead to formation of a metal *mono*thiocarbonate and a metal-*thio*carbonyl. But our results (*e.g.*, equation 7) indicate that C—S bound carbonyl sulphide ligands react with COS to give dithiocarbonates.[47] These products could arise from an electrophilic attack on the endocyclic sulphur atom by another COS molecule, followed by elimination of CO, as shown in Scheme 3.

Examples of metal-promoted disproportionations of CO_2,[35,37] CS_2,[59] RNCO,[60,61] RNCS,[51,62] and RNCNR[63] have been reported, and in each case

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[56] G. Fachinetti, C. Biran, C. Floriani, A. Chiesi-Villa, and C. Guastini, *J. Am. Chem. Soc.*, 1978, **100**, 1921.

[57] R. K. Poddar and U. Agarwala, *J. Coord. Chem.*, 1977, **6**, 207.

[58] M. Pasquali, C. Floriani, A. Chiesi-Villa, and C. Guastini, *Inorg. Chem.*, 1980, **19**, 3847.

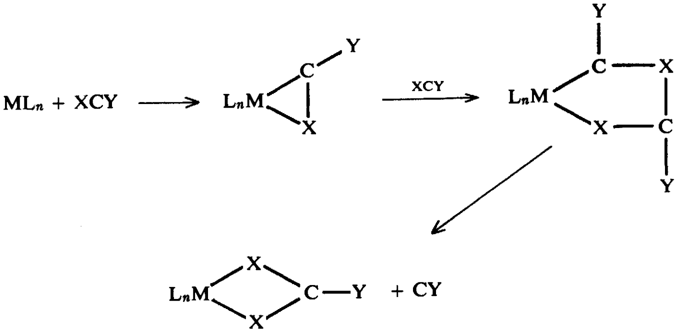
[59] D. H. M. W. Thewissen, *J. Organomet. Chem.*, 1980, **188**, 211.

[60] G. Fachinetti, C. Biran, C. Floriani, A. Chiesi-Villa, and C. Guastini, *J. Chem. Soc., Dalton Trans.*, 1979, 792.

[61] D. H. M. W. Thewissen, Ph.D. Thesis, Catholic University, Toernooiveld, The Netherlands, 1980, 102.

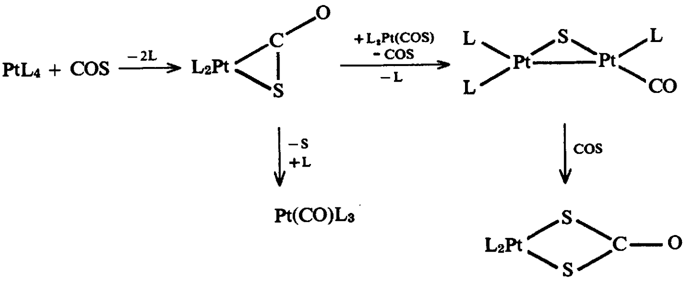
[62] D. H. M. W. Thewissen and H. L. M. van Gaal. *J. Organomet. Chem.*, 1979, **172**, 69.

[63] D. M. Duggan, *Inorg. Chem.*, 1979, **18**, 903.



Scheme 3

the intermediacy of a head-to-tail bis(hetero-allene) dimer has been proposed (Scheme 3). In instances where head-to-tail dimers have been isolated,[56,62,64,65] they are stable and do not rearrange. If the reaction shown in equation (8) proceeds by the mechanism depicted in Scheme 3, we would expect formation of the head-to-tail dimer to be fast, since Pt(η^2-COS)(PPh_3)$_2$ decomposes if allowed to stand in solution, and rearrangement of the head-to-tail dimer would be the rate-determining step. Our failure to detect and isolate this proposed intermediate, Pt$(COS)_2(PPh_3)_2$, leads us to believe that the reaction proceeds by the alternative mechanism shown in Scheme 4. Infrared and n.m.r. spectroscopic studies of the reaction are consistent with the proposed mechanism. The fact that the dithiocarbonate can be prepared from Pt$(PPh_3)_4$, Pt(η^2-COS)(PPh_3)$_2$,



Scheme 4

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[64] H. Werner, O. Kolb, R. Feser, and U. Schubert, *J. Organomet. Chem.*, 1980, **191**, 283.
[65] J. R. Schmidt and D. M. Duggan, *Inorg. Chem.*, 1981, **20**, 318.

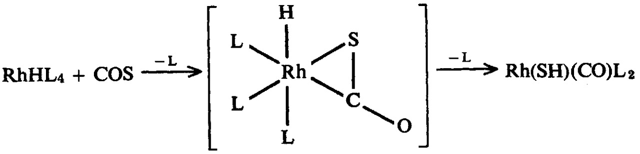
or $Pt_2S(CO)(PPh_3)_3$ by addition of COS is also consistent with the mechanism.

Carbonyl sulphide also may be a useful reagent for the formation of monothiocarbonates. Thus the dioxygen complexes $Pt(O_2)(PPh_3)_2$ and $Pd(O_2)(PPh_3)_2$ react with COS apparently to afford $Pt(CO_2S)(PPh_3)_2$ and $Pd(CO_2S)(PPh_3)_2$, the first examples of monothiocarbonato transition-metal complexes. With CS_2 these same dioxygen complexes afford $Pt(COS_2)(PPh_3)_2$ and $Pd(COS_2)(PPh_3)_2$[66] while $Pt(O_2)(PPh_3)_2$ with CO_2 affords a peroxycarbonate that decomposes to yield $Pt(CO_3)(PPh_3)_2$.[66]

We have presented examples of carbonylation involving COS as well as S abstraction from bound COS. These two processes converge in the very interesting reaction:[67]

$$RhH(PPh_3)_4 + COS \rightarrow Rh(SH)(CO)(PPh_3)_2 \qquad (9)$$

That the product of this reaction is the mercapto compound *trans*-$Rh(SH)(CO)(PPh_3)_2$ has been confirmed by infrared, ^1H, and $^{31}P\{^1H\}$ n.m.r. spectroscopy, and a crystal structure determination. A possible pathway of this reaction is shown in Scheme 5. Replacement of one PPh_3 ligand by COS could lead to a η^2-COS bound intermediate. Subsequent hydride transfer to sulphur and C—S bond cleavage could lead to the formation of $Rh(SH)(CO)(PPh_3)_2$. As we have demonstrated here, C—S bond cleavage in η^2-bound COS ligands is a facile process. Moreover, formation of mercapto ligands from metal sulphides and hydrogen has recently been reported.[68]



Scheme 5

Examples of CO_2 and CS_2 insertions into metal hydride bonds are numerous; such insertions invariably result in the formation of formate and dithioformate ligands.[1,4,69] There is no precedent for insertion of an O or S atom of CO_2, COS, or CS_2 into a metal hydride bond. Our results suggest that reactions that result in C—S bond cleavage in COS are competitive with simple insertions. Presumably, the weakening of the C—S bond upon co-ordination of COS to the metal centre, which is thought to be the first step in these hetero-allene

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[66] P. J. Hayward, D. M. Blake, G. Wilkinson, and C. J. Nyman, *J. Am. Chem. Soc.*, 1970, **92**, 5873.

[67] T. R. Gaffney and J. A. Ibers, submitted to *Inorg. Chem.*

[68] M. Rakowski DuBois, M. C. VanDerveer, D. L. DuBois, R. C. Haltiwanger, and W. K. Miller, *J. Am. Chem. Soc.*, 1980, **102**, 7456.

[69] D. J. Darensbourg, A. Rokicki, and M. Y. Darensbourg, *J. Am. Chem. Soc.*, 1981, **103**, 3223.

insertion reactions,[1] results in C—S bond cleavage. The reactions[70-73] of metal amides with CO_2 are catalysed by HNR_2 and are believed to involve initial formation of HO_2CNR_2 and subsequent reaction with the metal complex.[72] For the related reactions with COS, no decarbonylation is observed.[70-73] But since formation of the monothiocarbamate ligand would be expected to occur prior to attachment of COS to the metal centre, metal-promoted C—S bond cleavage would not be expected in these reactions.

The formal sulphur insertion reaction observed here for COS contrasts with the reactions of $RhH(PPh_3)_4$ with CO_2 and CS_2. The complex $RhH(PPh_3)_4$ reacts slowly with CO_2 to afford a carbonate-bridged dimer $Rh_2(CO_3)(PPh_3)_5$.[74] Although this reaction may involve cleavage of the hetero-allene bond (C—O) to form the carbonate ligand, it may also depend on the presence of adventitious water.[74] The complex $RhH(PPh_3)_4$ reacts rapidly with CS_2, but the analogous thiocarbonyl complex, $Rh(SH)(CS)(PPh_3)_2$, does not appear to be produced as we detect no CS stretching vibration in the infrared spectrum of the products.[67]

To provide some quantitative data on relative stabilities of CS_2 and COS complexes we[75] have determined the equilibrium constant of equation (10) for various phosphines and Y = O or S. No comparable data appear in the literature.

$$IrCl(CO)(L)_2 + SCY \rightleftharpoons IrCl(CO)(\eta^2\text{-}SCY)(L)_2 \qquad (10)$$

The complexes $IrCl(CO)(L)_2$ (L = PPh_3, $PMePh_2$, PMe_2Ph, or PMe_3) react with CS_2 to afford complexes in which the CS_2 molecule is bound to the metal through a C—S bond.[2,75,76] The CS_2 complexes with L = PPh_3 and $PMePh_2$ dissociate CS_2, even in the solid state, but for L = PMe_2Ph and PMe_3 the solids are stable under vacuum. The complexes with smaller, more basic phosphine ligands (L = PMe_2Ph or PMe_3) also react with COS to afford similar products, which dissociate COS in the solid state and in solution at room temperature. The equilibrium constant for equation (10) is readily established from the relative areas of the distinct $^{31}P\{^1H\}$ resonances of the two metal-containing species and from the concentration of SCY. Since the equilibrium constant could generally be measured between 15 and −22 °C, thermochemical constants for these reactions were derived and are listed in Table 3. The large equilibrium constant favouring the reaction of $IrCl(CO)(PMe_3)_2$ with CS_2 precluded the determination of values of ΔH and ΔS for this reaction.

If we assume that solvation effects are unimportant, the values of ΔH for equations (11) and (12) are a measure of the relative Ir(COS) and $Ir(CS_2)$ bond energies. From these data we estimate that the $Ir(CS_2)$ bond is 1.4 times as strong as the Ir(COS) bond. The principal bonding interaction in similar iridium com-

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[70] A. L. Arduini, J. D. Jamerson, and J. Takats, *Inorg, Chem.*, 1981, **20**, 2474.

[71] L. Busetto, A. Palazzi, and V. Foliadis, *Inorg. Chim. Acta*, 1980, **40**, 147.

[72] M. H. Chisholm and M. W. Extine, *J. Am. Chem. Soc.*, 1977, **99**, 782.

[73] M. H. Chisholm and M. W. Extine, *J. Am Chem. Soc.*, 1977, **99**, 792.

[74] S. Krogsrud, S. Komiya, T. Ito, J. A. Ibers, and A. Yamamoto, *Inorg. Chem.*, 1976, **15**, 2798.

[75] T. R. Gaffney and J. A. Ibers, *Inorg. Chem.*, in the press.

[76] A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A.*, 1969, 1128.

Table 3 *Thermodynamic constants for the equilibria (in toluene)*

$\mathrm{IrCl(CO)(L)_2 + SCY \rightleftharpoons IrCl(CO)(\eta^2\text{-}SCY)(L)_2}$

L	Y	K_{eq}(30 °C)/M^{-1}	ΔH/kcal mol^{-1}	ΔS/e.u.	*Equation number*
PMe_2Ph	O	1.7 ± 0.4*	-11.8 ± 1.1	-38 ± 5	11
PMe_2Ph	S	108 ± 20	-17.1 ± 2.5	-47 ± 9	12
PMe_3	O	12.9 ± 3	-13.1 ± 1.2	-38 ± 5	13
PMe_3	S	>1400	---	---	14

*Limit of error, determined graphically

plexes is thought to result from donation of electron density from the highest occupied molecular orbital of the $IrCl(CO)(L)_2$ complex to the lowest unoccupied molecular orbital of the ligand, as the stability of such complexes towards dissociation of the ligand increases with increasing electron affinity of the ligand.[77] Consistent with this are the electron affinities of Table 1. The values of K for equations (15) and (16) reflect this increase in stability that results from substitution of CS_2 for COS, and the values of ΔH and ΔS for equation (15) ($\Delta H = -5.3 \pm 2.7$ kcal mol^{-1}, $\Delta S = -9 \pm 10$ e.u.) suggest that it is the increase in enthalpy, and not entropy, that favours formation of the CS_2 complexes. Since the steric requirements of the COS and CS_2 complexes should be similar (for the same L), we believe this increased stability is primarily electronic in nature.

$$\begin{aligned}&\mathrm{IrCl(CO)(\eta^2\text{-}COS)(PMe_2Ph)_2 + CS_2 \rightleftharpoons}\\&\mathrm{IrCl(CO)(\eta^2\text{-}CS_2)(PMe_2Ph)_2 + COS}\quad K = 64\end{aligned}\tag{15}$$

$$\mathrm{IrCl(CO)(\eta^2\text{-}COS)(PMe_3)_2 + CS_2 \rightleftharpoons IrCl(CO)(\eta^2\text{-}CS_2)(PMe_3)_2 + COS}\quad K > 100\tag{16}$$

Equations (17) and (18) illustrate that formation of the CS_2 and COS complexes is favoured by smaller, more basic phosphine ligands.

$$\begin{aligned}&\mathrm{IrCl(CO)(\eta^2\text{-}COS)(PMe_2Ph)_2 + IrCl(CO)(PMe_3)_2 \rightleftharpoons}\\&\mathrm{IrCl(CO)(\eta^2\text{-}COS)(PMe_3)_2 + IrCl(CO)(PMe_2Ph)_2}\quad K = 7.6\end{aligned}\tag{17}$$

$$\begin{aligned}&\mathrm{IrCl(CO)(\eta^2\text{-}CS_2)(PMe_2Ph)_2 + IrCl(CO)(PMe_3)_2 \rightleftharpoons}\\&\mathrm{IrCl(CO)(\eta^2\text{-}CS_2)(PMe_3)_2 + IrCl(CO)(PMe_2Ph)_2}\quad K > 13\end{aligned}\tag{18}$$

Surely, steric as well as electronic factors are important here.

As we have demonstrated here, the chemistry of M-COS complexes is dominated by reactions that involve cleavage of the C—S bond, whereas analogous reactions of M-CS_2 complexes represent only a small fraction of the observed chemistry.[4,50] The reactions discussed here illustrate that the bonding interaction between $IrCl(CO)(L)_2$ complexes and COS is weaker than for CS_2, and that a more basic metal complex is needed to stabilize a M-COS complex than a M-CS_2 complex. Transfer of electron density from the basic metal centre to the π^* orbital of COS should weaken the C—S bond. But the bond

[77] R. N. Scott, D. F. Shriver, and L. Vaska, *J. Am. Chem. Soc.*, 1968, **90**, 1079.

energy of the C—S bond in COS is weaker than it is in CS_2 (Table 1), at least as judged by ΔH for the reaction:

$$CSY \rightarrow CY + S \qquad (19)$$

This need for a basic metal centre to stabilize M-COS bond formation and the destabilization of the weak C—S bond that results account for the paucity of M-COS complexes and the instability of those that have been prepared.

5 Summary

This brief excursion into the reactivities of CS_2, CO_2, and COS towards transition metals demonstrates the diversity of the individual chemistries. Although CS_2 is a very reactive molecule, CO_2 is not. Cleavage of the C—O bond in CO_2[78] and the C—S bond in CS_2 play only minor roles in the chemistries, whereas C—S bond cleavage in COS is the important aspect of the chemistry. Thus far, the study of COS chemistry has not proved directly helpful in the activation of CO_2. Nor has the use of liquid CO_2 led to new, stable CO_2 complexes. Yet COS chemistry has proved to be interesting and diverse in its own right, with potential applications to carbonylation reactions. And the use of liquid CO_2 has proved to be valuable as a screening technique for reactivity of transition-metal systems towards CO_2.

The chemistry of these molecules is in an early stage of development. Much remains to be explored, including a wider range of transition metals, kinetics and mechanisms of the reactions, and theoretical studies of the bonding. I am optimistic that the increased interest in this area, engendered in part by the potential utilization of CO_2 as a source for C_1 chemistry, will lead to rapid development of the chemistry of these fascinating molecules.

Acknowledgements. The CS_2 and CO_2 chemistry described here is the work of Dr. Michael G. Mason. The COS chemistry described here is that of Dr. Thomas R. Gaffney. It has been a privilege for me to be associated with two such talented young investigators. The loan of precious metals used in this study by Johnson-Matthey, Inc., Malvern, Pennsylvania and the support of this research by the U.S. National Science Foundation (CHE76-10335 and CHE80-09671) has made this work possible. I thank the Sherman Fairchild Distinguished Scholars Program of the California Institute of Technology under whose auspices this review was written.

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[78] T. Yoshida, D. L. Thorn, T. Okano, J. A. Ibers, and S. Otsuka, *J. Am. Chem. Soc.*, 1979, **101**, 4212.