DINUCLEAR METAL CARBONYLS

DINUCLEAR PHOSPHORUS- AND ARSENIC-BRIDGED CARBONYL COMPOUNDS

III*. PHOTOCHEMICAL REACTIONS WITH PHOSPHINES

D. T. THOMPSON
Imperial Chemical Industries Limited, Petrochemical and Polymer Laboratory, The Heath, Runcorn, Cheshire (England)

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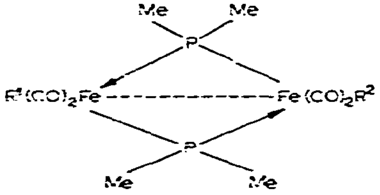
It is well known that the action of light on metal carbonyls can promote substitution reactions: for example, as early as 1905 Dewar and Jones[1] had prepared iron nonacarbonyl by the action of light on iron pentacarbonyl. Irradiation techniques have now been used to replace carbonyl groups by a variety of other groups such as olefines[2], acetylenes[2], π-allyl[2,3], nitrogen[2]- and sulphur[2]-containing ligands, and phosphines[2,4-6] and arsines[2].

The irradiation of some of the dinuclear metal carbonyls described in Parts I[7] and II[8] with visible light in the presence of trialkyl-, triaryl-, or bidentate phosphines is now reported. Irradiation with visible light of a cyclohexane solution of bis(μ-dimethylphosphido)bis(tricarbonyliron) (Ia) and triphenylphosphine (one or two equivalents) results in replacement of one (Complex Ib) or to a small extent of two carbonyl groups (Complex Ic). Use of one equivalent of triethylphosphine instead of the triphenylphosphine produces the monosubstituted complex (Id); but when two equivalents of triethylphosphine are used the disubstituted complex (Ie) is the principal product.



(I)

(a), $R^1 = R^2 = CO$; (b), $R^1 = PPh_3$, $R^2 = CO$; (c), $R^1 = R^2 = PPh_3$; (d), $R^1 = PEt_3$, $R^2 = CO$; (e), $R^1 = R^2 = PEt_3$.

When a benzene solution of (Ia) is irradiated in the presence of 1,2-bis(diphenylphosphino)ethane, two products are obtained. In one of these products, (II), two of the carbonyl groups in (Ia) have been replaced by the diphosphine; and in the other,

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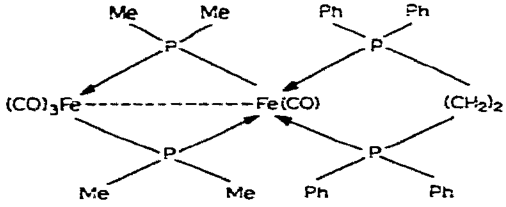
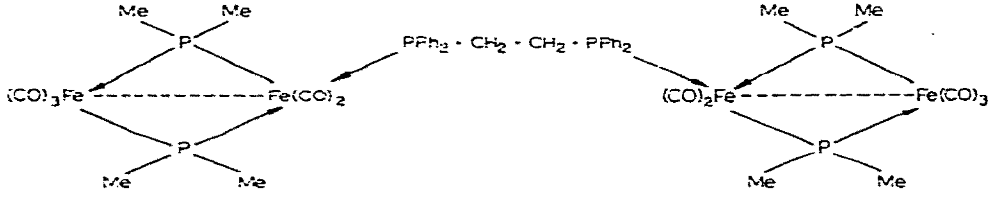
[*] For Part II see ref. 8.



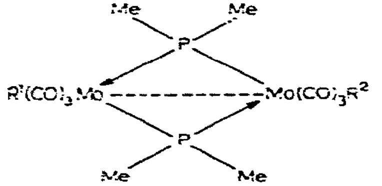
(II)

(III), one carbonyl group from each of two molecules of (Ia) appears to be replaced by the diphosphine to give a compound containing four metal atoms. Nyholm *et al.*[4,5] found that using their photochemical technique, a bidentate phosphine could be used to link two metal atoms together, but the compound (III) seems to be the first example in which two dinuclear fragments are linked by a diphosphine.



(III)

Irradiation of a benzene solution of bis(μ-dimethylphosphido)bis(tetracarbonylmolybdenum) (IVa) and triphenylphosphine with visible light gives the very insoluble compound (IVb) which is precipitated in a pure microcrystalline form from the reaction mixture. Even in the presence of a very large excess of triphenylphosphine, (IVb) is the only product isolated (73 % yield based on IVa) and there is no indication of further substitution. Substitution of triethylphosphine for triphenylphosphine in

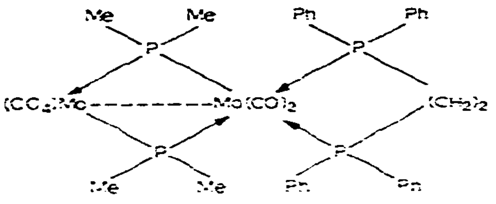


(IV)

(a), $R^1 = R^2 = CO$; (b), $R^1 = R^2 = PPh_3$; (c), $R^1 = R^2 = PEt_3$.

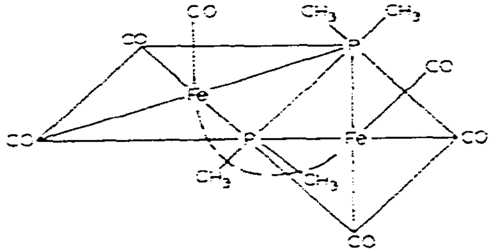
this reaction gives the more soluble product (IVc), crystallisable from benzene. No mono-substituted compound is produced in either of these experiments. When 1,2-bis(diphenylphosphino)ethane is used, the compound (V) is isolated in which two of the carbonyl groups in (IVa) have been replaced by the bidentate phosphine.

Both of our starting complexes (Ia and IVa) are diamagnetic and are therefore thought to have structures containing a metal–metal bond[7,8]. Lewis *et al.*[5] reported that, whereas the phosphines PPh_3 and PEt_3 react thermally with dimanganese


(V)

decacarbonyl to give only the paramagnetic monomers $Mn(CO)_4PR_3$ (R = Et, Ph), photochemical techniques give the diamagnetic dimers $[Mn(CO)_4PR_3]_2$ in which the metal–metal bonds remain intact. Heat alone is not effective in promoting our substitution reactions. Under irradiation, the metal–metal bonds remain intact even more readily than in the experiments of Lewis *et al.*, for in addition to the comparatively weak metal–metal bond there is strong bonding through the dimethylphosphido groups.

The assignment of structures for the compounds produced in our experiments presents an interesting problem. The structure (VI), in which the metal–metal bond is bent and occupies the vacant octahedral positions of the iron atoms, has been proposed by Hayter[9]. Structure (VI) is based on that of the similar compound $Fe_2(CO)_6(SEt)_2$, which has been determined by X-ray crystallography[10]. In the structure (VI) there are two carbonyl groups situated *trans* to a metal–metal bond, and four situated *trans* to phosphine groups. The preparative results indicate that with visible light two carbonyls are replaced by phosphine much more readily than are the other four. Even in the presence of six equivalents of phosphine, complex (Ia) gives no products involving substitution of any of the four remaining carbonyl groups. It therefore seems reasonable to conclude that with compound (Ia), having structure (VI), the carbonyls *trans* to the metal–metal bond are substituted by phosphines under visible light, and that this method cannot be used for substituting any of the other carbonyls; the complex (Ie) probably being formed more readily than (Ic) for steric reasons, it is difficult to accommodate the two large triphenylphosphine molecules in the space available, but relatively easy to accommodate two triethylphosphines. However, it can also be argued that two carbonyls *trans* to phosphines are replaced and the resulting compound deactivated towards further attack by the presence of the additional phosphines, but this seems less likely than the first explanation because it does not account for the difference in yield of disubstituted product when changing from triphenylphosphine to triethylphosphine (*i.e.* 0 to 44 %; Experiments 2 and 4, Table 1).

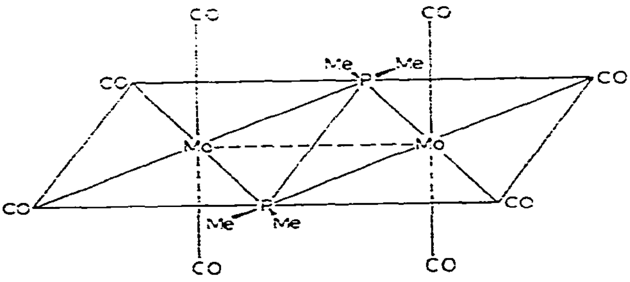

(VI)

Further, it was shown by thin-layer chromatography that compounds (Ib) and (Ic) are each homogeneous. If all the carbonyl groups in (Ia) were replaceable with equal ease, a mixture of isomers would be expected, and if the carbonyls *trans* to phosphines were the easiest to replace it is likely that at least two isomers would be produced. Our observations are thus consistent with compound (Ia) having the structure (VI), with the two carbonyls *trans* to the metal–metal bond being more susceptible to replacement by phosphine than the other four. However, the evidence for structure (VI) is not conclusive, and X-ray crystallography is being used to enable us to make a more definite assignment of structure to the compounds (I).

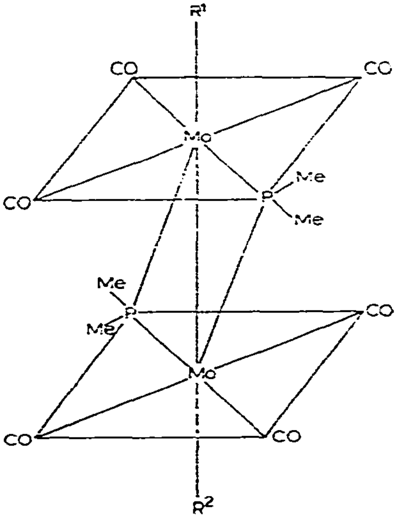
Since one and only one carbonyl group can be replaced from each molybdenum atom in the compound (IVa), it seems probable that one carbon monoxide molecule occupies a unique position on each atom. This is not in accord with structure (VII) and therefore structure (VIII) or (IX) is suggested. In structure (VIII) the molybdenum atom is given a pentagonal bipyramidal configuration in analogy with that suggested by Nigam, Nyholm and Stiddard[11] for [Mo(diarsine)(CO)$_3$I$_2$]. In analogy with the structure of the iron compound (VI), structures (VIII) and (IX) have the unique carbon monoxide group in a *trans*-position to the metal–metal bond.

The number of carbonyl bands observed in the infrared spectra (Table 2) of the products obtained is consistent with the structures proposed, and similar spectra are obtained from compounds with similar structures. The spectrum of complex (II) has bands of medium intensity at 794, 662 and 665 cm^{-1}; while that of (V) has medium bands at 806, 667 and 648 cm^{-1}; these bands can be assigned to the CH$_2$ groups of the chelating diphosphine and since none of these bands is present in the spectrum of compound (III) where the chelating diphosphine is symmetrically situated, the structures (II) and (V) are preferred to the more symmetrical structures (X) and (XI).

With 1,2-bis(diphenylphosphino)ethane, (Ia) produces two products but (IVa)



(VII)



(VIII)

(a), R^1 = R^2 = CO; (b), R^1 = R^2 = PPh$_3$; (c), R^1 = R^2 = PEt$_3$.

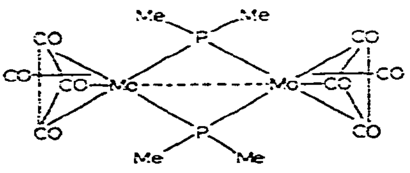
TABLE I

PHOTO-REPLACEMENT OF CARBONYL GROUPS IN DINUCLEAR COMPLEXES BY PHOSPHINE GROUPS

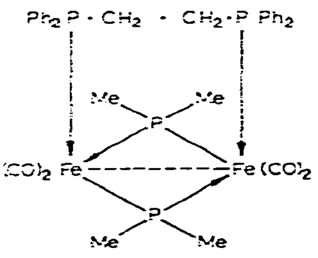
No.	*Starting complex (g)*	*Phosphine (no. of equivalents)*	*Solvent (ml)*	*Time irradiated (h)*	*Product A (% yield)*	*Description (m.p., °C)*	*Analysis (%)*	
							Calcd.	*Fo*
1	(Ia) (4.00)	PPh_3 (1)	Cyclohexane (400)	218	(Ib) (26)	Orange-red prisms (162–166)	C 51.0 H 4.3 P 14.6	51. 4. 14.
2	(Ia) (5.45)	PPh_3 (2)	Cyclohexane (220)	220	(Ib) (23)			
3	(Ia) (4.00)	PEt_3 (1)	Benzene (200)	257	(Id) (21)	Yellow-orange prisms (115–120)	C 36.6 H 5.5 P 18.9	36. 5. 18.
4	(Ia) (2.00)	PEt_3 (2)	Benzene (200)	211	(Ie) (44)	Yellow-orange needles (120–125)	C 41.3 H 7.3 P 21.3	41. 7. 20.
5	(Ia) (3.04)	$(PPh_2CH_2)_2$ (1)	Benzene (360)	47	(III) (2)	Yellow prisms (260 dec.)	C 46.1 H 4.2 P 16.2	46. 4. 15.
6	(Ia) (1.94)	$(PPh_2CH_2)_2$ (1)	Benzene (200)	210	(III) (2)			
7	(IVa) (1.03)	PPh_3 (8)	Benzene (200)	120	(IVb) (73)	Light red prisms (200 dec.)	C 54.9 H 4.2 P 12.3	55. 4. 13.
8	(IVa) (3.00)	PEt_3 (2)	Benzene (260)	226	(IVc) (44)	Orange flakes (192–193)	C 36.8 H 5.9 P 17.2	36. 5. 17.
9	(IVa) (2.05)	$(PPh_2CH_2)_2$ (1)	Benzene (350)	232	(V) (46)	Yellow prisms (230–250)	C 49.1 H 4.1 P 14.1	49. 4. 14.

[a] Dipole moments were determined in benzene using Chatt and Thornton's method[7]. [b] Dete ebullioscopically. [c] Determined using V.P. osmometer.

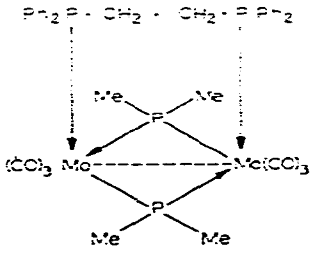
gives only one. If the first step of the reaction with the iron compound is assumed to involve the replacement of one of the carbonyl groups *trans* to a metal–metal bond by one end of the diphosphine, then the second phosphorus atom has a choice between



(IX)



(X)



(XI)

e nt^a	*Molecular weight*		*Product B (% yield)*	*Description (m.p., °C)*	*Analysis (%)*		*Dipole moment^a (D)*	*Molecular weight*	
	Calcd.	*Found*			*Calcd.*	*Found*		*Calcd.*	*Found*
	636	660^c	(Ic) (1)	Red prisms (200)	C 60.7 H 4.9 P 14.2	60.9 5.4 14.8			
			None						
	492	471^b							
	582	571^b							
	1146	1122^c							
			(II) (17)	Purple needles (235–238)	C 54.9 H 4.9 P 16.6	54.8 4.9 16.5	6.77	744	800^c
	718	690^c							
	880	830^b							

TABLE 2

INFRARED SPECTRA OF POLYNUCLEAR METAL COMPLEXES IN CHLOROFORM SOLUTION

s, strong; m, medium; w, weak; b, broad.

Compound	*Carbonyl frequencies*	*Compound*	*Carbonyl frequencies*
(Ia)	2051 (w), 2008 (s), 1975^b (m), 1966 (m)	(III)	2015 (m), 1961 (s), 1949 (s), 1913 (m)
(Ib)	2022 (m), 1964 (s), 1935^b (m), 1900^b (w)	(IVa)	2026 (m), 1958 (s)
(Ic)	1975 (s), 1936 (s), 1915 (m), 1885^b (m)	(IVb)	1966^a (w), 1930^a (w), 1902^a (s), 1890^{a,b}
(Id)	2022 (m), 1959 (s), 1932^b (m), 1905^b (w)	(IVc)	1963^a (m), 1900^{a,b} (s), 1887^a (s)
(Ie)	1996 (m), 1958 (s), 1919 (s), 1900^b (m)	(IVc)	1964 (w), 1896 (s)
(II)	1997 (s), 1927 (s, b), 1885 (m)	(V)	2021 (m), 1916 (s, b), 1844 (w)

^{a} KBr disc. ^{b} Inflection.

displacing a carbonyl group *trans* to a phosphine, a carbonyl group *trans* to a metal–metal bond but which is situated in an unfavourable position sterically, or a carbonyl group *trans* to a metal–metal bond which is sterically favoured but depends on a suitable molecular collision. In practice the phosphorus atom chooses the first and third of these possibilities, in that order. With the molybdenum compound the second phosphorus atom has a similar series of choices, except that the second phosphorus can displace a carbonyl on the same side of the molecule *trans* to another carbonyl (Structure VIII) since this is a more favoured process than displacing a carbonyl *trans* to a phosphine, and is much more favourable than displacing a carbonyl from another molecule, only one product (V) is isolated, and in high yield compared with the corresponding iron compound.

EXPERIMENTAL

Irradiation experiments

Irradiation experiments were performed in deoxygenated solvents under an atmosphere of dry, oxygen-free nitrogen in "Pyrex" apparatus using "Spectosun" lamps fitted with 118 V (625 W) iodine–quartz bulbs. Details of the experiments are given in Table 1. A solution of the dinuclear carbonyl complex and the phosphine was irradiated for the time shown. With the iron compounds, solvent was removed from the product under reduced pressure, and the residue dissolved in the minimum of benzene and added to an alumina (Spence "Type H")/light petroleum (b.p. 40–60°) column (4 × 80 cm). Elution with light petroleum removed unchanged starting material. Elution with light petroleum–benzene afforded the crude products, which were purified by crystallisation from benzene–light petroleum. With the molybdenum compounds, the products were removed by filtration and recrystallised (if possible) from benzene. The infrared spectra of the products are summarised in Table 2. For microanalysis the molybdenum compounds were burnt in the presence of potassium dichromate.

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SUMMARY

When solutions of dinuclear metal carbonyls are irradiated with visible light in the presence of trialkyl- or triarylphosphines, carbonyl groups situated in positions *trans* to metal–metal bonds are replaced by the phosphine but carbonyl groups *trans* to phosphines or to other carbonyls are not attacked. When 1,2-bis(diphenylphosphino)ethane is used instead of the monophosphine a number of products can be formed and evidence for the structures of these derivatives is adduced.

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