Oxidative Additions to Stable Five-co-ordinate d^8 Complexes: Bis[1,2-bis(diphenylphosphino)ethane]- and Bis[1,2-bis(diphenylphosphino)ethylene]-(isocyanide)iridium(I) Complexes

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The stable, five-co-ordinate, cationic species $[Ir(CNR)L_2]^+$ [R = Me or *p*-MeC_6H_4; L = 1,2-bis(diphenylphosphino)ethane (dppe) or 1,2-bis(diphenylphosphino)ethylene (dppen)] undergo oxidative addition of *proton acids (including methanol)*, halogens, and $HgCl_2$ *without* loss of a ligand to give dicationic adducts $[IrY(CNR)L_2]^{2+}$ (Y = H, Cl, I, or HgCl), but do not react with alkyl, allyl, or acyl halides. Proton acids give *cis*-adducts under kinetic control which may then isomerize on heating. Dihydrogen and dioxygen react very slowly to give *cis*-$[IrH_2L_2]^+$ and $[Ir(O_2)L_2]^+$, respectively and SO_2 gives an unstable adduct which dissociates at room temperature even in liquid SO_2.

FIVE-CO-ORDINATE d^8 complexes, $[ML_5]^{z+}$, usually undergo oxidative addition of addenda (XY) by one of the following mechanisms.[1] The complex either dissociates to a four-co-ordinate species which then undergoes addition of XY [equation (1)], or it displaces X^- from the

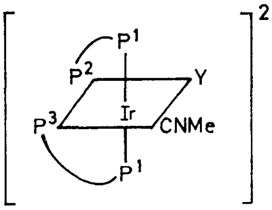
$$[ML_5]^{z+} \xrightarrow{-L} [ML_4]^{z+} \xrightarrow{XY} [MX(Y)L_4]^{z+} \qquad (1)$$

addendum to give an ionic intermediate from which L is then displaced by X^- [equation (2)]. Only in a few cases

$$[ML_5]^{z+} + XY \longrightarrow [M(Y)L_5]^{(z+1)+} + X^- \longrightarrow [MX(Y)L_4]^{z+} + L \qquad (2)$$

has the ionic intermediate of reaction (2) been isolated, *viz.* in the addition of HX to $[CoH(dppe)_2]$,[2] $[Os(CO)_3(PPh_3)_2]$,[3] $Os(CO)_5$,[4] $[Ru(CNR)(CO)_2(PPh_3)_2]$,[5] $[IrH(CO)(PPh_3)_3]$,[6] $[IrH(CO)_2(PPh_3)_2]$,[7] and $[M(CNR)_3(PPh_3)_2]^+$ (M = Rh and Ir, R = alkyl or aryl),[8] of X_2 (X = Cl, Br, and I) to $[Os(CO)_3(PPh_3)_2]$,[9] of MeI to $[Rh(CNBu^t)_3(PPh_3)_2]^+$,[8] and of $HgCl_2$ to $[M(CO)_3(PPh_3)_2]$ (M = Fe,[10] Ru, and Os [11]).

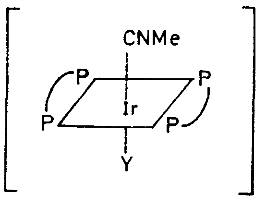
We have now synthesized the five-co-ordinate complexes $[Ir(CNR)L_2]^+$ [R = Me or *p*-MeC_6H_4; L = 1,2-bis(diphenylphosphino)ethane (dppe) or *cis*-1,2-bis(diphenylphosphino)ethylene (dppen)] in which the five donor atoms are held so tenaciously that neither the first step of reaction (1) nor the second step of (2) can proceed. Isocyanides appear to be among the most powerful unidentate ligands known, at least towards metal ions of the d^8 configuration. Thus methyl isocyanide displaces all the ligands in $[IrCl(CO)(PPh_3)_2]$ [12] and $[Ir(CO)(pdma)_2]^+$ [pdma = *O*-phenylenebis(dimethylarsine)] to give $[Ir(CNMe)_4]^+$, and in $[\{RhCl(CO)_2\}_2]$ [13] and $[RhCl(cod)_2]$ [14] (cod = η-cyclo-octa-1,5-diene) to give $[Rh(CNMe)_4]^+$. The *cis*-isocyanide groups in Chugaev's cation $[Pt(C_4H_9N_4)(CNMe)_2]^+$ are displaced by CN^- and dppe but not by pdma, 1,10-phenanthroline (phen), or CO.[15] Complexes $[Ir(CNR)L_2]^+$ readily add addenda XY to give stable, doubly charged, cationic species $[IrY(CNR)L_2]^{2+}$ which, at least when Y = H, have configuration (I) and are formed under kinetic control. Analytical data for the new iridium(I) and iridium(III) complexes are given in Table 1 and their spectroscopic properties are summarized in Table 2.



(I)

RESULTS AND DISCUSSION

The Complexes $[Ir(CNR)L_2]^+$.—Methanol solutions of the blue complex $[Ir(CNMe)_4]^+$ [12] did not react with dppe in the dark but photosubstitution occurred rapidly in light to give yellow $[Ir(CNMe)(dppe)_2]^+$. The same product was formed on treating $[IrH(CNMe)(dppe)_2]^{2+}$ of configuration (I), but not of configuration (II), with base and, in high yield, on treating $[IrCO(dppe)_2]^+$ [16,17] with an excess of methyl isocyanide at room temperature. It is best isolated as the crystalline perchlorate; the complexes $[Ir(CNMe)(dppen)_2][ClO_4]$ and $[Ir(CNC_6H_4Me\text{-}p)(dppe)_2][ClO_4]$ were obtained in a similar way but



(II)

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TABLE 1

Analytical data (%) and conductivities for new iridium complexes

	Λ	Found				Calc.			
	S cm^2 mol^{-1}	C	H	N	Cl	C	H	N	Cl
$[Ir(CNMe)(dppe)_2][ClO_4]$	110 [a] 92 [b]	57·3	4·6	1·3		57·4	4·55	1·2	
$[Ir(HgCl)(CNMe)(dppe)_2][ClO_4]_2,H_2O$	260 [a]	43·8	3·5	0·9	7·4	43·7	3·6	0·9	7·2
$[IrI(CNMe)(dppe)_2][ClO_4]_2,H_2O$	250 [a]	47·2	4·0	1·2		47·2	3·9	1·0	
$[IrCl(CNMe)(dppe)_2][ClO_4]_2$	250 [a]	51·6	4·2	1·2		51·3	4·1	1·1	
$[IrH(CNMe)(dppe)_2][BF_4]_2,H_2O$ (I)	270 [a]	52·8	4·2	1·45		53·0	4·45	1·15	
$[IrH(CNMe)(dppe)_2][ClO_4]_2,H_2O$ (II)	240 [a]	52·0	4·4	1·0	5·1	52·0	4·4	1·1	5·7
$[Ir(CNMe)(dppen)_2][ClO_4]$	130 [a]	57·1	4·2	1·3		57·6	4·2	1·2	
$[Ir(HgCl)(CNMe)(dppen)_2][ClO_4]_2,H_2O$	270 [a]	43·9	3·4	0·95		43·85	3·3	0·95	
$[IrI(CNMe)(dppen)_2][ClO_4]_2,H_2O$	270 [a]	47·8	3·9	1·0		47·35	3·6	1·0	
$[IrH(CNMe)(dppen)_2][BF_4]_2,H_2O$ (I)		53·2	4·1	1·1		53·2	4·1	1·15	
$[Ir(CO)(pdma)_2][ClO_4]$		26·5	3·3			28·3	3·6		
$[Ir(HgCl)(CO)(pdma)_2][HgCl_4]$		18·5	2·4			18·4	2·35		
$[Ir(CNC_6H_4Me\text{-}p)(dppe)_2][ClO_4],\frac{1}{2}MeOH$	130 [a]	59·5	5·0	0·8		59·5	4·7	1·15	
$[Ir(HgCl)(CNC_6H_4Me\text{-}p)(dppe)_2][ClO_4]_2$		47·9	4·4	1·1		46·8	3·6	0·9	
$[IrCl(CNC_6H_4Me\text{-}p)(dppe)_2][ClO_4]_2,H_2O$	270 [a]	53·0	4·9	1·4		53·0	4·2	1·0	
$[IrH(CNC_6H_4Me\text{-}p)(dppe)_2][ClO_4]_2$ (I)	270 [a]	55·35	4·4	1·0		55·2	4·3	1·1	

[a] In acetonitrile (10^{-3}M). [b] In methanol (10^{-3}M).

TABLE 2

I.r. (cm^{-1}) and ^{1}H n.m.r. data for the new iridium complexes

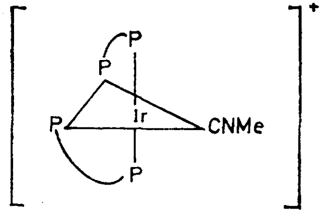
Complex	ν(C–N)	Other bands	$\tau(CH_3)$	$\tau(CH_2)$	τ(IrH)	Solvent (n.m.r.)
$[Ir(CNMe)(dppe)_2][ClO_4]$	2 127s		7·23 (q); J(P–H) 1·5 Hz	7·82 (m)		Dichloromethane
			7·19 (q)			$[^2H_3]$Acetonitrile
$[Ir(HgCl)(CNMe)(dppe)_2][ClO_4]_2,H_2O$	2 234s	305m ν(HgCl)]	6·20 (s)	6·20 (m)		Nitrobenzene
			6·77 (s)	6·77 (m)		$[^2H_3]$Acetonitrile
			6·32 (s)	6·32 (m)		Pyridine
$[Ir(HgCl)(CNMe)(dppe)_2][BPh_4]_2$	2 225s		7·07 (s)	7·15 (m)		$[^2H_6]$Acetone
$[IrI(CNMe)(dppe)_2][ClO_4]_2,H_2O$	2 246s		6·49 (s)	6·70 (m)		$[^2H_3]$Acetonitrile
$[IrI(CNMe)(dppe)_2][BPh_4]_2$	2 246s		6·41 (s)	6·67 (m)		$[^2H_6]$Acetone
			7·32 (s)	7·45 (m)		Dichloromethane
$[IrCl(CNMe)(dppe)_2][ClO_4]_2$	2 246s	303m [ν(IrCl)]	6·65 (s)	6·6 (m)		Liquid SO_2
cis-$[IrH(CNMe)(dppe)_2][BF_4]_2,H_2O$	2 249s	2 112m [ν(IrH)]	7·29 (s)	7·48 (m)	20·7 (ddt); J(P–H) 117, 15·6, and 10·2 Hz	$[^2H_3]$Acetonitrile
cis-$[IrH(CNMe)(dppe)_2][ClO_4]_2,H_2O$	2 250s	2 110m [ν(IrH)]	7·29 (s)	7·3 (m)	20·8 (ddt); J(P–H) 117, *ca.* 10, and *ca.* 10 Hz	$[^2H_3]$Acetonitrile
trans-$[IrH(CNMe)(dppe)_2][BF_4]_2,H_2O$	2 242s		6·87 (s)	7·4 (m)	21·08 (q); J(P–H) 13 Hz	$[^2H_3]$Acetonitrile
trans-$[IrH(CNMe)(dppe)_2][ClO_4]_2,H_2O$	2 238s		6·86 (s)	7·3 (m)	21·8 (q)	$[^2H_3]$Acetonitrile
trans-$[IrH(CNMe)(dppe)_2][BPh_4]_2$			6·95 (s)	7·4 (m)	22·0 (q); J(P–H) 13·2 Hz	$[^2H_3]$Acetonitrile
			6·71 (s)	7·2 (m)	21·7 (q)	$[^2H_6]$Acetone
$[Ir(CNMe)(dppen)_2][ClO_4]$	2 148s		7·63 (q); J(P–H) 1·2 Hz	[a]		Dichloromethane
			7·57 (q); J(P–H) 1·3 Hz			$[^2H_1]$Chloroform
$[Ir(HgCl)(CNMe)(dppen)_2][ClO_4]_2,H_2O$	2 250s		7·08 (s)	[a]		$[^2H_3]$Acetonitrile
$[IrI(CNMe)(dppen)_2][ClO_4]_2,H_2O$	2 263s		6·77 (s)	[a]		$[^2H_3]$Acetonitrile
cis-$[IrH(CNMe)(dppen)_2][BF_4]_2,H_2O$	2 254s	2 100m [ν(IrH)]	7·55 (s)	[a]	20·5 (ddt); J(P–H) 118, 14·8, and 10·2 Hz	$[^2H_3]$Acetonitrile
			7·42 (s)	[a]	20·5 (ddt)	Liquid SO_2
$[Ir(CNC_6H_4Me\text{-}p)(dppe)_2][ClO_4]$	2 063s 2 038s		7·75 (s)	7·7 (m)		$[^2H_3]$Acetonitrile
	2 077 [b] 2 038s		7·73 (s)	7·7 (m)		$[^2H_1]$Chloroform
$[Ir(HgCl)(CNC_6H_4Me\text{-}p)(dppe)_2][ClO_4]_2,H_2O$	2 183s		7·61 (s)	6·66 (m)		$[^2H_3]$Acetonitrile
$[IrI(CNC_6H_4Me\text{-}p)(dppe)_2][ClO_4]_2,H_2O$	2 198s					
$[IrCl(CNC_6H_4Me\text{-}p)(dppe)_2][ClO_4]_2$	2 220s	303m [ν(IrCl)]	7·54 (s)	6·65 (m)		$[^2H_3]$Acetonitrile
cis-$[IrH(CNC_6H_4Me\text{-}p)(dppe)_2][ClO_4]_2,H_2O$	2 196s	2 147m [ν(IrH)]	7·67 (s)	7·1 (m)	20·3 (ddt); J(P–H) 118, 15·4, and 10·2 Hz	$[^2H_3]$Acetonitrile
$[Ir(CO)(pdma)_2][ClO_4]$		1 936s [ν(CO)]				
$[Ir(HgCl)(CO)(pdma)_2][HgCl_4]$		2 070s [ν(CO)]				

s = Strong, and m = medium (i.r.); s = singlet, q = quintet, ddt = doublet of doublet of triplets, and m = multiplet (n.m.r.).
[a] Obscured by phenyl resonance. [b] Chloroform solution.

[Ir(CNMe)(pdma)$_2$] could not be isolated. When [IrCO(pdma)$_2$][ClO$_4$], obtained from *trans*-[IrCl(CO)(PPh$_3$)$_2$] and pdma, was heated with methyl isocyanide (1 mol) it gave a mixture of [Ir(CNMe)$_4$][ClO$_4$] and unreacted [IrCO(pdma)$_2$][ClO$_4$]. The related complex [Rh(CNBu^t)(dppe)$_2$][BF$_4$] had been obtained previously.[18]

The complexes [Ir(CNR)L$_2$][ClO$_4$] analysed correctly for this formulation for R = Me and L = dppe and dpen, but [Ir(CNC$_6$H$_4$Me-*p*)(dppen)$_2$][ClO$_4$] retained half a molecule of methanol, even *in vacuo* over P$_2$O$_5$, which could be detected in both the i.r. and n.m.r. spectra. Conductivities in acetonitrile were those expected for 1 : 1 electrolytes (Table 1). The solids were stable indefinitely and could be recrystallized from methanol without reaction, but solutions oxidized slowly in air. Whereas [IrCO(dppe)$_2$]$^+$ [15,16] and [IrCO(dppen)$_2$]$^+$ [19,20] readily lose carbon monoxide on heating *in vacuo*, [Ir(CNMe)(dppe)$_2$][ClO$_4$] retained MeNC tenaciously and a sample underwent no change after heating *in vacuo* at 150—160 °C for 2 h or 180—190 °C for 0·5 h. The complex [IrCO(pdma)$_2$]Br is said to lose CO on heating,[21] but we could not confirm this and [IrCO(pdma)$_2$][ClO$_4$] was recovered after heating the solid *in vacuo* or a suspension in boiling xylene under an argon atmosphere.

The C≡N stretching frequencies in the i.r. spectra occurred at 2 127 (R = Me, L = dppe), 2 148 (R = Me, L = dppen), and 2 050 and 2 038 cm^{-1} (R = *p*-MeC$_6$H$_4$, L = dppe), *lower* than in the free isocyanide by 43, 22, and 76 cm^{-1} respectively. The band in [Ir(CNC$_6$H$_4$Me-*p*)(dppe)$_2$][ClO$_4$] was split even in solution (CHCl$_3$), presumably as a result of Fermi resonance with the first overtone of a band at *ca.* 1 100 cm^{-1}. The low C≡N stretching frequency indicates substantial metal to ligand π-bonding [22,23] and resistance of the co-ordinated isocyanide to nucleophilic attack.[12,23] In keeping with this the complexes failed to react with sodium methoxide, ethylamine, or *p*-toluidine under mild conditions. The methyl resonance in the n.m.r. spectra of [Ir(CNMe)(dppe)$_2$]$^+$ and [Ir(CNMe)(dppen)$_2$]$^+$ at τ 7·23 and 7·63 was a 1 : 4 : 6 : 4 : 1 quintet both at 60 and 100 MHz, due to coupling to four equivalent ^{31}P nuclei [^5J(PH) = 1·6 and 1·3 Hz, respectively]. Such long-range coupling over five bonds is very unusual and is absent from other MeNC complexes such as [OsCl$_2$(CNMe)(PR$_3$)$_3$],[24] [OsCl(CNMe)$_2$(PR$_3$)$_3$]$^+$,[23] [Rh(CNMe)$_2$(PR$_3$)$_3$]$^+$, [Rh(CNMe)$_3$(PR$_3$)$_2$]$^+$,[8] and the adducts of [Ir(CNMe)L$_2$]$^+$. Reformulation as [IrMe(CN)L$_2$]$^+$ is excluded by the chemical properties of these complexes, so that the quintet structure is consistent only with the rigid (overlapping triplet of triplets) or non-rigid trigonal-bipyramidal geometry of configuration (III) or with a square-pyramidal geometry with apical MeNC. We were unable to alter the structure of the methyl resonance by cooling a dichloromethane solution to −60 °C and we obtained no information from the ^{31}P n.m.r. spectrum (a broad singlet at 100 MHz). Molecular models have shown that the barrier to interconversion of the two isomers of [CoCl(dppe)$_2$]$^+$ by a Berry-type mechanism is high,[25] and [Ir(CNMe)L$_2$]$^+$ might thus also be expected to be rigid. By analogy with the known structure of [IrCO(dppe)$_2$]Cl [26] we cautiously suggest configuration (III) for the isocyanide complexes. A single-crystal *X*-ray study of [Ir(CNMe)(dppe)$_2$][ClO$_4$] has been undertaken.[27]



(III)

Additions of Acids, Halogens, and Mercury(II) *Chloride.*—The complexes [Ir(CNR)(dppe)$_2$]$^+$ reacted immediately with proton acids (HCl, MeCO$_2$H, and H$_2$SO$_3$), Cl$_2$, I$_2$, and HgCl$_2$ to give colourless or pale yellow adducts [IrY(CNR)L$_2$]$^{2+}$ (Y = H, Cl, I, and HgCl; R = Me and *p*-MeC$_6$H$_4$; L = dppe. Y = H, I, and HgCl; R = Me; L = dppen). The perchlorates and tetrafluoroborates analysed mostly as monohydrates and in such cases water bands were detected in the i.r. spectra. Conductivities in acetonitrile were those expected for 2 : 1 electrolytes (Table 1). The complex [Ir(CNMe)(dppe)$_2$][ClO$_4$] did not react with methyl iodide, n-butyl iodide, allyl halides, or diphenylacetylene. It dissolved in pure acetyl chloride without reaction and, after standing for several hours, the solution deposited a small amount of [IrH(CNMe)(dppe)$_2$][ClO$_4$]$_2$, presumably formed from traces of moisture. Tetracyanoethylene gave a mixture of products which could not be characterized.

The hydride resonance in the ^{1}H n.m.r. spectrum of [IrH(CNMe)(dppe)$_2$][BF$_4$]$_2$ was a doublet of a doublet of triplets centred at τ 20·7 at both 60 and 100 MHz. Hence the adduct has the *cis*-configuration (I) with J(P^1–H) 15·6, J(P^2–H) 10·2, and J(P^3–H) 117 Hz. The large P–H coupling constant is characteristic of hydride *trans* to a phosphine.[28] The Ir–H stretching frequency occurred at 2 112 cm^{-1}. When the *cis*-adduct was heated in methanol at 90 °C for 20 h it gave a white isomer with no Ir–H stretch in the i.r. spectrum but with a hydride resonance at τ 21·8 which was a 1 : 4 : 6 : 4 : 1 quintet. Hence the product is *trans*-[IrH(CNMe)(dppe)$_2$][BF$_4$]$_2$ of configuration (II). Thus protonation evidently occurs under ***kinetic*** control since it gives the thermodynamically

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less-stable isomer. Protonation of $[Ir(CNMe)(dppen)_2]^+$ and $[Ir(CNC_6H_4Me\text{-}p)(dppe)_2]^+$ also gave adducts of configuration (I), but *cis*-$[IrH(CNC_6H_4Me\text{-}p)(dppe)_2]^{2+}$ did not isomerize on heating in methanol. Whereas *cis*-$[IrH(CNMe)(dppe)_2]^{2+}$ reacted rapidly with sodium methoxide to give $[Ir(CNMe)(dppe)_2]^+$, the *trans*-isomer did not react in the cold. We could not establish the configuration of $[IrY(CNMe)(dppe)_2]^{2+}$ (Y = Cl, I, and HgCl) unequivocally, but the much greater width of the methylene resonances in the adducts compared to $[Ir(CNMe)(dppe)_2]^+$ suggests that these adducts probably also have configuration (I). The adducts (Y = Cl, I, and HgCl) were unchanged after heating in methanol at 90 °C for several days, but $[IrI(CNMe)(dppe)_2][BPh_4]_2$ was reduced to $[Ir(dppe)_2][BPh_4]$ when heated in 2-methoxyethanol under reflux for 2 h. The product separated on cooling as large red prisms.

The methyl n.m.r. spectrum of all the adducts was a singlet at τ 6·2—7·5 and occurred alone in the dppen complexes but superimposed on a complex methylene multiplet in the dppe complexes. The C≡N stretching frequency in the iridium(III) adducts occurred 100—120 cm^{-1} higher than in the iridium(I) precursors and 50—90 cm^{-1} higher than in the free isocyanides, suggesting [22] that isocyanide acts predominantly as a σ-donor in the adducts. The co-ordinated isocyanide function should therefore be moderately reactive towards nucleophiles.[12,23] Nevertheless, the adducts failed to react with methanol or *p*-toluidine under mild conditions, and were recovered. Their reactivity towards stronger nucleophiles is currently under investigation. A strong band at 303 cm^{-1} in the i.r. spectra of $[IrCl(CNR)(dppe)_2][ClO_4]_2$ (R = Me and *p*-MeC_6H_4), but absent from $[Ir(CNR)(dppe)_2][ClO_4]$ and $[IrI(CNR)(dppe)_2][ClO_4]_2$, is assigned to the Ir–Cl stretch. The Hg–Cl stretch in $[Ir(HgCl)(CNMe)(dppe)_2][ClO_4]_2$ occurred at 305 cm^{-1} and a weak band at 157 cm^{-1} in the Raman is possibly due to the Ir–Hg stretch. Addition of $HgCl_2$ to $[IrCO(pdma)_2][ClO_4]$ [ν(CO) at 1 936 cm^{-1}] yielded white crystals of $[Ir(HgCl)CO(pdma)_2][HgCl_4]$ [ν(CO) at 2 070 cm^{-1}], but addition of HCl and I_2 gave a mixture of products.

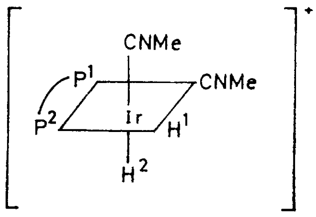
Reaction of $[Ir(CNMe)(dppe)_2][ClO_4]$ *with Methanol.*—The complex $[Ir(CNMe)(dppe)_2][ClO_4]$ did not react with methanol at 100 °C for 48 h, but on prolonged heating (2—6 weeks at 100 °C) it was partly converted to *trans*-$[IrH(CNMe)(dppe)_2][ClO_4]_2$. The reaction proceeded to completion at room temperature in 1 a. We found no evidence for the formation of either methoxide or carbene complexes in this system and no dihydrogen could be detected by Raman spectroscopy in reactions carried out in Carius tubes. The solutions became strongly alkaline indicating the presence of methoxide ion. We therefore suggest that methanol acts as an acid towards $[Ir(CNMe)(dppe)_2]^+$ to give *cis*-$[IrH(CNMe)(dppe)_2]^{2+}$ and MeO^-, but with the equilibrium lying heavily to the left. This is followed by slow isomerization of the *cis*- and the *trans*-adduct which no longer reacts with MeO^- [equations (3) and (4)]. No new iridium complexes were obtained

$$[Ir(CNMe)(dppe)_2]^+ + MeOH \rightleftharpoons cis\text{-}[IrH(CNMe)(dppe)_2]^{2+} + MeO^- \quad (3)$$

$$cis\text{-}[IrH(CNMe)(dppe)_2]^{2+} \rightleftharpoons trans\text{-}[IrH(CNMe)(dppe)_2]^{2+} \quad (4)$$

on heating with RI (R = Me and Bu^n) in methanol but iodide ion was liberated, presumably from the reaction of MeO^- with RI. These results are analogous to the reaction of $[Ir(CO)(dmpe)_2]^+$ with methanol to give $[IrH(O_2CMe)(dmpe)_2]^+$ [dmpe = 1,2-bis(dimethylphosphino)ethane], but where MeO^- formed initially attacks co-ordinated CO.[29] It has been reported that $[Ir(CNBu^t)_3(PPh_3)_2]^+$ reacts with methanol to give $[Ir(OMe)(CNBu^t)_3(PPh_3)_2]^{2+}$,[8] but in the absence of n.m.r. data it is possible that this is also a hydride complex.

Reaction of $[Ir(CNR)L_2]^+$ *with Dihydrogen, Dioxygen, and Sulphur Dioxide.*—In all cases so far reported, saturated d^8 complexes either add H_2, O_2, or SO_2 by reaction (1), or are inert.[1] Solutions of $[Ir(CNMe)(dppe)_2][ClO_4]$ in acetonitrile reacted only very slowly with dihydrogen and addition was still incomplete after 3 d under a pressure of 3 atm. The only products which could be detected were *cis*-$[IrH_2(dppe)_2][ClO_4]$ {the hydride resonance was a doublet of multiplets at τ 21·7, J[P(*trans*)–H] 110 Hz} and free methyl isocyanide. The complex *cis*-$[IrH_2(dppe)_2][ClO_4]$ did not itself react with excess of methyl isocyanide at room temperature even after 3 weeks incubation. Under the same conditions, but in the presence of a ten-fold excess of methyl isocyanide, $[Ir(CNMe)(dppe)_2][ClO_4]$ gave $[IrH_2(CNMe)_2(dppe)][ClO_4]$ of configuration (IV) [the hydride resonances were a triplet at τ 22·92, $J(P\text{–}H^2)$ 16·2 Hz, and a doublet of doublets at τ 20·5, $J(P^1\text{–}H^1)$ 125, $J(P^2\text{–}H^1)$ 13·8 Hz], and free dppe. It therefore appears that the rate-determining step is dissociation of a donor atom and that in the presence of excess of methyl isocyanide dissociation of dppe competes successfully with dissociation of co-ordinated MeNC.



(IV)

Solutions of $[Ir(CNMe)(dppe)_2][ClO_4]$ reacted *slowly* with dioxygen to give the known [16,17] complex $[Ir(O_2)(dppe)_2][ClO_4]$ in low yield, together with some $Ph_2(O)PCH_2CH_2P(O)Ph_2$. The complex $[Ir(O_2)(dppe)_2][ClO_4]$ did not itself react with excess of methyl isocyanide even on heating. It could be isolated in two polymorphs, α and β, with distinct *X*-ray powder patterns. The α polymorph crystallized from methanol in rhombic prisms and the β polymorph from benzene–methanol in needles.

Although crystalline adducts of sulphur dioxide were

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[29] S. D. Ibekwe and K. A. Taylor, *J. Chem. Soc.* (*A*), 1970, 1.

not isolated, n.m.r. evidence showed that weak, six-co-ordinate, solvates were formed in liquid SO_2 at low temperatures. The orange solution of $[Ir(CNMe)(dppen)_2][ClO_4]$ in liquid SO_2 at room temperature had a quintet at τ 7·60 [^5J(P–H) 1·4 Hz] at 100 MHz, characteristic of free $[Ir(CNMe)(dppen)_2]^+$. As the temperature was lowered the solution became deep red and the methyl resonance gradually moved downfield and broadened to a singlet. At *ca.* −40 °C a new broad signal appeared at τ 7·77 which sharpened as the temperature was lowered further, so that at −70 °C the solution, again orange, gave two sharp signals of roughly equal intensity at τ 6·73 and 7·74. The same changes occurred in reverse when the solution was allowed to warm up. Methyl resonances in solutions of $[Ir(CNMe)(dppe)_2][ClO_4]$ were obscured by methylene resonances. These results may be interpreted on the basis of the fast equilibrium (5)

$$[Ir(CNMe)(dppen)_2]^+ + SO_2 \rightleftharpoons [Ir(SO_2)(CNMe)(dppen)_2]^+ \quad (5)$$

which lies heavily to the left at room temperature and becomes slower and shifts progressively towards the right as the temperature is lowered. The SO_2 adducts are evidently too unstable to form at room temperature. It is interesting that $[Ir(CNBu^t)_3(PPh_3)_2]Cl$ is reported to form a crystalline adduct $[Ir(SO_2)(CNBu^t)_3(PPh_3)_2]Cl$.[8] If this is in fact the case it would be the only instance in which a saturated d^8 complex forms a *stable* adduct with SO_2.

EXPERIMENTAL

C, H, and N Analyses were made by the Microanalytical Laboratory, National Physical Laboratory, Teddington, and Cl analyses by A. Bernhardt, Mikroanalytisches Laboratorium, Mülheim. All samples were dried over phosphorus penta-oxide at 10^{-2} mmHg before analysis. I.r. spectra were recorded in Nujol mulls on Perkin-Elmer 337 or a Unicam SP 200G spectrometers, unless otherwise stated, and far-i.r. spectra on Perkin-Elmer 225 or Beckman IR11 spectrometers. ^{1}H N.m.r. spectra were recorded on Perkin-Elmer R12 (60 MHz) or Varian HA100 instruments (100 MHz). Conductivities were measured with a Philips PR 9500 conductance bridge.

All reactions were carried out under an argon atmosphere unless otherwise stated and all solvents were degassed. Methyl [30] and *p*-tolyl isocyanide [31] were prepared by published methods. The phosphine dppe was prepared by the method of Chatt and Hart (second method) [32] and dppen by a similar method.[33] The complex *trans*-$[IrCl(CO)(PPh_3)_2]$ was prepared by a modification of a literature method [34] in which the product was heated with sodium methoxide (0·3 mol) to reduce the accompanying $[IrH(Cl)_2(CO)(PPh_3)_2]$; $[Ir(CO)(dppe)_2]Cl$ was prepared by the method of Vaska and Catone [16] and $[Ir(CO)(dppen)_2]Cl$ was prepared similarly [19] except that the reaction required several hours to proceed to completion.

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*](*methyl isocyanide*)*iridium*(I) *Perchlorate.*—*Method* (a). A solution of $[Ir(CNMe)_4]Cl$ (0·50 g) in methanol (30 cm^3) was treated with dppe (1·00 g) in benzene (5 cm^3). The solution remained deep blue in the dark but became yellow almost immediately on irradiation with light from a quartz–iodine lamp. After irradiation for 5 min in the cold, the solution was heated with sodium perchlorate (0·5 g), taken to dryness, and the residue washed with benzene and methanol. The product was recrystallized from aqueous methanol to give the *salt* as yellow prisms (0·94 g, 65%), readily soluble in acetone, chloroform, dichloromethane, and acetonitrile, sparingly soluble in cold methanol and ethanol, and insoluble in water and benzene.

Method (b). A solution of $[Ir(CO)(dppe)_2]Cl$ (5·0 g) in methanol was treated with methyl isocyanide (0·4 g, 2 mol. equiv.) in methanol in the cold. The solution immediately became yellow and bright yellow prisms of the *salt* (4·6 g, 88%) separated on addition of sodium perchlorate (5 g) in methanol. The product was recrystallized from methanol.

Method (c). A solution of *cis*-$[IrH(CNMe)(dppe)_2][ClO_4]_2,H_2O$ (0·028 g) in methanol was stirred with sodium methoxide (0·001 g) for 20 min and then evaporated to dryness. The residue was recrystallized from methanol to give the *salt*.

Bis[cis-1,2-*bis*(*diphenylphosphino*)*ethylene*](*methyl isocyanide*)*iridium*(I) *Perchlorate and Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*](*p-tolyl isocyanide*)*iridium*(I) *Perchlorate.*—These complexes were prepared in the same way as $[Ir(CNMe)(dppe)_2][ClO_4]$ in *ca.* 90% yield. The methyl isocyanide complex was recrystallized from methanol and the *p*-tolyl isocyanide complex from acetone–methanol.

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*](*chloromercurio*)(*methyl isocyanide*)*iridium*(III) *Salts.*—(a) *Perchlorate.* The complex $[Ir(CNMe)(dppe)_2][ClO_4]$ (0·40 g), dissolved or suspended in methanol, was treated with mercury(II) chloride (0·1 g, 1 mol. equiv.) and stirred until it became colourless. Sodium perchlorate (0·1 g) in methanol was added slowly to precipitate the *complex* (0·44 g, 85%), which was then recrystallized from methanol–ethanol as white prisms of the monohydrate. The salt is readily soluble in acetonitrile, nitrobenzene, and pyridine but sparingly soluble in other common solvents.

(b) *Tetraphenylborate.* (*i*) $[Ir(HgCl)(CNMe)(dppe)_2][ClO_4]_2,H_2O$ (0·1 g) was dissolved in hot methanol in air and sodium tetraphenylborate (0·09 g) in methanol was added with stirring. After stirring for a further hour the white granular precipitate of the *complex* (0·089 g, 75%) was recrystallized from acetonitrile–ethanol. It is readily soluble in acetone. (*ii*) $[Ir(CNMe)(dppe)_2]Cl$ was prepared *in situ* from $[Ir(CO)(dppe)_2]Cl$ (0·30 g) and methyl isocyanide (0·025 g) in methanol, excess of methyl isocyanide was removed under reduced pressure, and the product was redissolved in methanol. Mercury(II) chloride (0·077 g, 1 mol. equiv.) was then added, followed by enough hot methanol to redissolve the initial precipitate of the tetrachloromercurate(II) salt of the adduct, and the solution was then treated with sodium tetraphenylborate (0·25 g) to yield a white precipitate of the complex.

Bis[cis-1,2-*bis*(*diphenylphosphino*)*ethylene*](*chloromercurio*)(*methyl isocyanide*)*iridium*(III) *Perchlorate and Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*](*chloromercurio*)(p-*tolyl isocyanide*)*iridium*(III) *Perchlorate.*—Both salts were prepared in a similar way to $[Ir(HgCl)(dppe)_2][ClO_4],H_2O$ in *ca.* 90% yield and are soluble in acetonitrile.

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*iodo*(*methyl isocyanide*)*iridium*(III) *Salts.*—(a) *Perchlorate.* The complex

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[30] R. E. Schuster, J. E. Scott, and J. R. Casanova, *Org. Synth.*, 1966, **46**, 75.

[31] L. Ugi and R. Meyr, *Org. Synth.*, 1961, **41**, 101.

[32] J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1960, 1378.

[33] A. M. Aguiar and D. Daigle, *J. Amer. Chem. Soc.*, 1964, **86**, 2299.

[34] J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.* (*A*), 1967, 604.

$[Ir(CNMe)(dppe)_2]ClO_4$(0·20 g) in acetone or dichloromethane was treated with iodine (0·044 g, 1 mol. equiv.) in acetone. Pale yellow crystals of the *salt* (0·18 g, 74%) separated on addition of sodium perchlorate (0·05 g) and concentration of the solution, and were recrystallized from acetone or dichloromethane. The complex is readily soluble in acetonitrile but sparingly soluble in dichloromethane, methanol, and acetone.

(b) *Tetraphenylborate.* The complex $[Ir(CNMe)(dppe)_2]$Cl, prepared *in situ* from $[Ir(CO)(dppe)_2]Cl$ (0·30 g), was treated with iodine (0·072 g, 1 mol. equiv.) in methanol, followed by sodium tetraphenylborate (0·5 g). The resulting yellow *precipitate* was washed with methanol. It is readily soluble in acetone. *Bis*[cis-1,2-*bis*(*diphenylphosphino*)*ethylene*]*iodo*(*methyl isocyanide*)*iridium*(III) *perchlorate* and *bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*iodo*(p-*tolyl isocyanide*)*iridium*(III) *perchlorate* were prepared similarly. They are readily soluble in acetonitrile, sparingly in acetone, methanol, and dichloromethane.

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*chloro*(*methyl isocyanide*)*iridium*(III) *Perchlorate*.—A solution of $[Ir(CNMe)(dppe)_2]ClO_4$ (0·10 g) in methanol was titrated with a solution of chlorine in carbon tetrachloride until the colour was just discharged. White crystals of the *complex* (0·087 g, 78%) separated on addition of sodium perchlorate (0·1 g) and were washed with methanol. The complex is readily soluble in acetonitrile and liquid sulphur dioxide. *Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*chloro*(p-*tolyl isocyanide*)*iridium*(III) *perchlorate* (85%) was obtained similarly and is soluble in acetonitrile and dichloromethane but not in acetone or methanol.

cis-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*hydrido*(*methyl isocyanide*)*iridium*(III) *salts*.—(a) *Perchlorate.* The complex $[Ir(CNMe)(dppe)_2][ClO_4]$ (0·20 g) in methanol was titrated with dry hydrogen chloride in methanol until the colour of the solution was discharged. Sodium perchlorate (0·05 g) was then added to give white crystals of the *salt* (0·185 g, 84%), which is moderately soluble in acetonitrile but otherwise sparingly soluble.

(b) *Tetrafluoroborate.* The complex $[Ir(CNMe)(dppe)_2]Cl$, prepared *in situ* from $[Ir(CO)(dppe)_2]Cl$ (0·20 g) and methyl isocyanide (0·17 g), was titrated with hydrogen chloride in methanol. Addition of sodium tetrafluoroborate (0·3 g) gave a white crystalline precipitate of the *complex* (0·20 g, 86%) which was washed well with methanol. The tetrafluoroborate is more soluble in acetonitrile, acetone, methanol, and dichloromethane than the perchlorate. cis-*Bis*[cis-1,2-*bis*(*diphenylphosphino*)*ethylene*]*hydrido*(*methyl isocyanide*)*iridium*(III) *tetrafluoroborate* and cis-*bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*hydrido*(p-*tolyl isocyanide*)*iridium*(III) *perchlorate* were prepared in a similar way in 55 and 85% yield, respectively, and have similar solubilities.

trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*hydrido*(*methyl isocyanide*)*iridium*(III) *Perchlorate* and *Tetrafluoroborate*.—The corresponding *cis*-complexes were heated at 100 °C in methanol for 20 h in evacuated sealed tubes. They separated on cooling as *prisms*, and are readily soluble in acetonitrile. The tetrafluoroborate is more soluble than the perchlorate.

Carbonylbis[o-*phenylenebis*(*dimethylarsine*)]*iridium*(I) *Perchlorate*.—A solution of *trans*-$[IrCl(CO)(PPh_3)_2]$ (0·68 g) in benzene was treated with pdma (0·5 g, 2 mol. equiv.) in benzene. A white gummy solid separated, and was dissolved in ethanol. White crystals of the *complex* (0·67 g, 86%) separated on addition of excess of sodium perchlorate and were recrystallized from acetone–diethyl ether. The complex is readily soluble in acetone and acetonitrile.

Carbonyl(*chloromercurio*)*bis*[o-*phenylenebis*(*dimethylarsine*)]*iridium*(III) *Tetrachloromercurate*(II).—A solution of $[Ir(CO)(pdma)_2][ClO_4]$ (0·05 g) in methanol was heated with mercury(II) chloride (0·06 g, 4 mol. equiv.) in methanol in the cold. A white precipitate of the *complex* (0·05 g, 55%) formed immediately, and is virtually insoluble in all common solvents.

Reactions of $[Ir(CNMe)(dppe)_2][ClO_4]$.—*With acetyl chloride.* Dry $[Ir(CNMe)(dppe)_2][ClO_4]$ (1 g) was placed in a fired, all glass, apparatus and dissolved in degassed acetyl chloride, freshly distilled *in vacuo*. The apparatus was sealed and the yellow solution was allowed to stand. The colour of $[Ir(CNMe)(dppe)_2]^+$ persisted for at least 12 h but a small amount of *cis*-$[IrH(CNMe)(dppe)_2][ClO_4]_2$ separated and was identified by i.r. and n.m.r. spectroscopy. No adduct of MeCOCl was obtained.

With dioxygen. A solution of the complex in benzene–methanol was allowed to stand in air for 1 d. A large excess of benzene was then added and the solution allowed to stand for a further 3 d when large orange-brown needles and a small amount of white crystals of *trans*-$[IrH(CNMe)(dppe)_2][ClO_4]_2$ [ν(CN) at 2 238 cm^{-1}] were deposited. The brown needles were separated mechanically and were recrystallized from methanol as rhombic prisms or from benzene–methanol as needles [ν(CN) absent; ν(O_2) at 846 cm^{-1}. Found: C, 55·9; H, 4·2; N, 0. Calc. for $C_{54}H_{48}ClIrO_6P_4$: C, 55·7; H, 4·3; N, 0%]. A sample of $[Ir(O_2)(dppe)_2]Cl$ (0·05 g) in acetonitrile did not react when heated with methyl isocyanide (0·11 g, 25 mol. equiv.) at 100 °C for 24 h.

With dihydrogen. The complex (0·25 g) in acetonitrile (10 cm^3) was shaken for 3 d under a dihydrogen atmosphere (3 atm). The solution eventually became nearly colourless and smelled strongly of free methyl isocyanide. The pale yellow residue left on evaporation had i.r. bands consistent with a mixture of *cis*-$[IrH_2(dppe)_2][ClO_4]$ and unreacted $[Ir(CNMe)(dppe)_2][ClO_4]$. It was recrystallized from acetone to yield white crystals of pure *cis*-$[IrH_2(dppe)_2][ClO_4]$ whose i.r. and n.m.r. spectra were identical to a sample prepared from $[Ir(dppe)_2][ClO_4]$ and dihydrogen. A solution of *cis*-$[IrH_2(dppe)_2][ClO_4]$ in [$^2H_3$]acetonitrile containing a ten-fold excess of free methyl isocyanide had n.m.r. peaks consistent with a mixture of its components only, even after incubating at room temperature for 3 d.

The complex $[Ir(CNMe)(dppe)_2][ClO_4]$ (0·76 g) and excess of methyl isocyanide (0·45 cm^3, 10 mol. equiv.) in acetonitrile was shaken for 3 d under a dihydrogen atmosphere (3 atm). A small amount of white crystals of dppe [together with traces of $Ph_2(O)PCH_2CH_2P(O)Ph_2$] were deposited and more dppe was extracted with light petroleum. The acetonitrile layer was evaporated to dryness to give a pale yellow residue of crude $[IrH_2(CNMe)_2(dppe)_2][ClO_4]$ (0·52 g, 100%), soluble in most organic solvents except benzene, diethyl ether, and saturated hydrocarbons. It was purified by reprecipitation from chlorobenzene–cyclohexane and ethylene glycol–aqueous sodium perchlorate, but could not be crystallized (Found: C, 48·9; H, 4·6; N, 3·4. Calc. for $C_{30}H_{32}ClIrN_2O_4P_2$: C, 46·5; H, 4·2; N, 3·6%). The i.r. spectrum had peaks at 2 241 and 2 220 [ν(CN)] and 2 016 cm^{-1} [ν(Ir–H)].

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