Reaction of Halide Ion with $[Cr(CO)_2(\eta\text{-}C_6Me_6)(NO)][PF_6]$: Stabilisation of the Product by Phosphine Substitution and *X*-Ray Crystal Structure of *trans,trans*-$[Cr(I)(CO)_2(PPh_2Me)_2(NO)]$

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Addition of halide ion, X^-, to $[Cr(CO)_2(\eta\text{-}C_6Me_6)(NO)][PF_6]$ affords red solutions from which, on addition of phosphorus donor ligands, L, may be isolated $[Cr(X)(CO)_2(L)_2(NO)]$. The identities of two carbonylnitrosyl species present in the intermediate red solutions are discussed with reference to the crystal structure of *trans,trans*-$[Cr(I)(CO)_2(PPh_2Me)(NO)]$; crystals are monoclinic, space group $P2_1$, with $Z = 2$ in a unit cell of dimensions $a = 9.796(4)$, $b = 18.019(8)$, $c = 8.968(1)$ Å, $\beta = 116.96(3)°$. The structure was solved from diffractometer data by the heavy-atom method, and refined to R 0.055 for 2 233 observed reflections.

WE have previously shown that H^-, D^-, or Me^- reacts with $[Cr(CO)_2(\eta\text{-arene})(NO)]^+$ to afford the neutral species $[Cr(CO)_2(\eta\text{-cyclohexadienyl})(NO)]$ by nucleophilic attack at the co-ordinated arene. In addition, halide ion (X^-) reacts with the cation to afford red solutions, the i.r. spectra of which are not incompatible with the presence of halogenocyclohexadienyl complexes.[1] As halogenocyclohexadienyl complexes have not previously been prepared we have investigated more fully the reaction between $[Cr(CO)_2(\eta\text{-}C_6Me_6)(NO)]^+$ and X^- ($X = Cl$, Br, or I). We now report that the red solutions formed probably contain species in which the arene has been displaced by nucleophilic attack at the metal. Although the red species have not been isolated they react with phosphorus ligands, L, to give $[Cr(X)(CO)_2(L)_2(NO)]$ which have a *trans*-dicarbonyl, *trans*-bisphosphine octahedral structure as shown by an *X*-ray structural study on $[Cr(I)(CO)_2(PPh_2Me)_2(NO)]$.

RESULTS

Synthetic Studies.—Addition of tetra-alkylammonium or tetraphenylphosphonium halides to $[Cr(CO)_2(\eta\text{-}C_6Me_6)(NO)][PF_6]$ in CH_2Cl_2 gives red solutions, the i.r. spectra of which show two carbonyl and one nitrosyl absorptions. For example, $[Pr^n_4N]Cl$ yields a solution with bands at 2 031, 1 953, and 1 697 cm^{-1}. The absorptions appear at frequencies lower than those of the dicarbonylnitrosyl cation suggesting the possibility that the product is a neutral cyclohexadienyl complex. The spectra of the red solutions set aside under nitrogen gradually change so that after several hours only one carbonyl and one nitrosyl absorption are apparent. Thus, in the case of the solution formed by chloride addition the final spectrum shows bands at 2 060 and 1 753 cm^{-1}. During the spectral change no change in the colour of the solution is noticeable.

Attempts to isolate either of the species present in the red solutions have been unsuccessful, although a number of solvents, including dichloromethane, acetone, ethanol, and liquid sulphur dioxide have been used to carry out the reactions. For example, warming a liquid SO_2 solution of $[Cr(CO)_2(\eta\text{-}C_6Me_6)(NO)][PF_6]$ and $[NMe_4]I$ to the boiling point caused the initial yellow colour to change to deep red. After removal of the solvent, recrystallisation from dichloromethane–hexane afforded red crystals which, however, were a mixture of the two red species and which rapidly decomposed in the air. Our inability to isolate the red species

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[1] N. G. Connelly and R. L. Kelly, *J.C.S. Dalton*, 1974, 2334.

then led us to attempt to identify them in solution; the reaction between $[Cr(CO)_2(\eta\text{-}C_6Me_6)(NO)][PF_6]$ and $[PPh_4]I$ was therefore monitored by ^1H n.m.r. spectroscopy in CD_3NO_2. At room temperature in a sealed tube, the initial spectrum showed one singlet at τ 7.52 due to the co-ordinated arene of the cation. As the red colouration developed, no evidence for the generation of the distinctive spectrum of the hexamethylcyclohexadienyl group was obtained. Instead, a singlet at τ 7.78 (due to free C_6Me_6) was the only new signal apparent throughout the reaction. It thus seems likely that reaction of $[Cr(CO)_2(\eta\text{-}C_6Me_6)(NO)]^+$ with halide ion results in rapid displacement of the arene.

Addition of phosphorus donor ligands to the red solutions in CH_2Cl_2 causes a rapid colour change to yellow-brown and gives, in the case of unidentate ligands, an i.r. spectrum showing only one carbonyl and one nitrosyl absorption. The products of the reactions are, however, more easily isolated from ethanol. Thus, addition of $[PPh_3Me]I$ to a suspension of $[Cr(CO)_2(\eta\text{-}C_6Me_6)(NO)][PF_6]$ gave a red solution and a white precipitate of $[PPh_3Me][PF_6]$. On filtration, and addition of PPh_3 a yellow-brown solution formed which gave a yellow solid when set aside. The corresponding reactions involving PPh_2Me, $PPhMe_2$, and $P(OPh)_3$ gave products of a similar nature (Table 1) whereas $Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2$ (diphos) gave very low yields of a compound of similar appearance but which exhibited two carbonyl bands at 2 022 and 1 964, and one nitrosyl band at 1 675 cm^{-1}.

TABLE 1

I.r., analytical, and m.p. data for the complexes $[Cr(I)(CO)_2(L)_2(NO)]$

L	M.p./°C	Yield (%)	Analyses[a] (%) C	H	N	$\bar{\nu}(CO)/cm^{-1}$ [b]	$\bar{\nu}(NO)/cm^{-1}$ [b]
PPh_3	>100[c]	37	57.9 (57.8)	4.3 (3.8)	1.8 (1.8)	1 969	1 685
PPh_2Me	>109[c]	45	50.6 (50.5)	4.0 (3.9)	2.0 (2.1)	1 963	1 673
$PPhMe_2$	>97[c]	19	40.0 (40.0)	3.9 (4.1)	2.8 (2.6)	1 957	1 669
$P(OPh)_3$	107	28	51.4 (51.5)	3.4 (3.4)	1.5 (1.6)	2 007	1 715

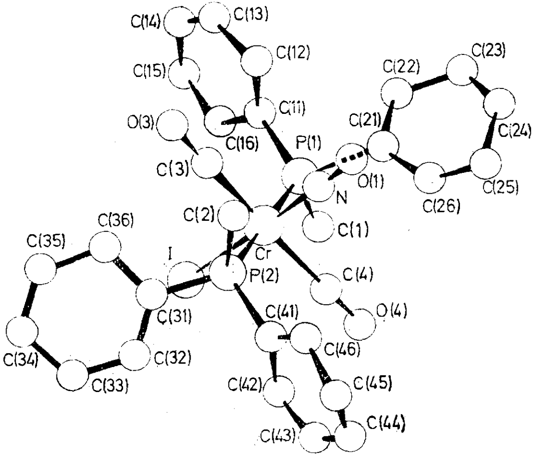
[a] Calculated values are given in parentheses. [b] In CH_2Cl_2. [c] Decomp.

The characterisation of the new phosphine ligand derivatives by microanalytical and spectral methods proved somewhat inconclusive. C, H, and N analyses were consistent with either $[Cr(I)(CO)_2(L)_2(NO)]$ or $[Cr(I)(CO)(L)_2(NO)]_2$ but attempts to measure molecular weights, by either mass-spectral or osmometric methods, in order to distinguish between mono- and di-meric products proved fruitless. The formation of halogen-bridged dimers *via* arene-displacement by halide ion is not without precedent: $[Mn(CO)_3(\eta\text{-arene})]^+$, isoelectronic with $[Cr(CO)_2(\eta\text{-}C_6Me_6)(NO)]^+$, reacts with I^- to give $[Mn(\mu\text{-}I)(CO)_4]_2$,[2] and $[M(CO)_3(\eta\text{-arene})]$ (M = Cr, Mo, or W) reacts with X^- (X = F, Cl, Br, or I) to yield $[M_2(\mu\text{-}X)_3(CO)_6]^{3-}$.[3] Neither the i.r. spectra of the complexes in the carbonyl and nitrosyl regions nor ^1H n.m.r. studies were of use in unequivocal structural assignment, although the ^1H n.m.r. spectrum of the iodobis(diphenylmethylphosphine) complex showed an apparent doublet at τ 7.65 ($|J_{PH} + J_{P'H}| = 8$ Hz), suggesting the presence of *cis*-phosphine ligands. In order to distinguish finally between the possible structural arrangements an *X*-ray study on the product from the reaction of $[Cr(CO)_2(\eta\text{-}C_6Me_6)(NO)][PF_6]$ with I^- and PPh_2Me was carried out.

Crystallographic Investigation.—The *X*-ray diffraction analysis (Tables 2 and 3) establishes the chemical identity of the crystals as $[Cr(I)(CO)_2(PPh_2Me)_2(NO)]$ in which the phosphine ligands are mutually ***trans***, and the carbonyl ligands likewise have a ***trans*** configuration. The chromium atom is in almost ideal octahedral co-ordination, and the carbonyl and nitrosyl groups are all approximately linear. There are no surprising features about the dimensions of the molecule: the principal bond lengths [Cr–I 2.75, Cr–P 2.40 (mean), Cr–N 1.70, Cr–C 1.90 (mean), C–O 1.14 (mean), N–O 1.12 Å] are all within expected ranges.[4,5] Details of the geometry of the phenyl rings have not therefore been included in Table 3; the mean C–C(Ph) distance is 1.38_8 Å and the mean C–C–C(Ph) angle 120°. The angles between the bonds to the three groups on the phosphorus atoms are all less than the ideal tetrahedral value. The carbonyl ligands bend slightly towards the iodine atom, to make the nitrosyl–chromium–carbonyl angles significantly more than 90°.

DISCUSSION

The *X*-ray characterisation (see Figure) of the new complexes as *trans,trans*-$[Cr(I)(CO)_2(L)_2(NO)]$ allows some speculation on the identities of the species present in the red solutions formed from $[Cr(CO)_2(\eta\text{-}C_6Me_6)(NO)][PF_6]$ and X^-. If, as seems likely, neither carbonyl nor nitrosyl ligands are displaced throughout the reaction sequence, then the initial red dicarbonylnitrosyl complex formed



Molecular structure of *trans,trans*-$[Cr(I)(CO)_2(PPh_2Me)(NO)]$

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[2] A. Davison and D. L. Reger, *J. Organometallic Chem.*, 1970, **23**, 491.

[3] J. F. White and M. F. Farone, *J. Organometallic Chem.*, **1972**, **37**, **119**.

[4] 'International Tables for *X*-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham.

[5] N. G. Connelly, *Inorg. Chim. Acta Rev.*, **1972**, **6**, 47.

TABLE 2

Atomic positional (fractional co-ordinates) and thermal parameters, with estimated standard deviations in parentheses

Atom	x	y	z	10^2U/Å^2 *
Cr	0.5776(2)	0.3369(1)	0.3016(2)	†
I	0.4545(1)	0.2500(fixed)	0.4621(1)	†
N	0.6469(13)	0.3913(6)	0.1957(13)	†
O(1)	0.6892(14)	0.4259(6)	0.1219(14)	†
C(3)	0.3752(15)	0.3496(8)	0.1334(15)	†
O(3)	0.2509(13)	0.3569(7)	0.0310(14)	†
C(4)	0.7748(17)	0.3182(7)	0.4879(19)	†
O(4)	0.8904(13)	0.3017(8)	0.5917(14)	†
P(1)	0.6073(4)	0.2255(2)	0.1758(4)	†
C(1)	0.687(2)	0.144(1)	0.309(2)	†
C(11)	0.429(2)	0.190(1)	−0.001(2)	4.0(3)
C(12)	0.367(2)	0.233(1)	−0.151(2)	5.3(4)
C(13)	0.230(2)	0.209(1)	−0.282(2)	7.6(5)
C(14)	0.162(2)	0.145(1)	−0.261(2)	6.7(5)
C(15)	0.218(2)	0.106(1)	−0.125(2)	6.3(4)
C(16)	0.358(1)	0.128(1)	0.018(2)	5.9(4)
C(21)	0.745(1)	0.232(1)	0.090(1)	3.5(3)
C(22)	0.724(2)	0.199(1)	−0.062(2)	4.5(3)
C(23)	0.837(2)	0.202(1)	−0.112(2)	4.8(3)
C(24)	0.972(2)	0.235(1)	−0.020(2)	5.1(4)
C(25)	0.998(2)	0.270(1)	0.135(2)	5.6(4)
C(26)	0.882(2)	0.268(1)	0.182(2)	4.4(3)
H(12)	0.424	0.245	−0.032	‡
H(13)	0.181	0.241	−0.381	‡
H(14)	0.067	0.127	−0.353	‡
H(15)	0.236	0.089	−0.012	‡
H(16)	0.324	0.088	−0.063	‡
H(22)	0.677	0.196	0.013	‡
H(23)	0.818	0.181	−0.217	‡
H(24)	1.036	0.248	0.096	‡
H(25)	1.045	0.272	0.058	‡
H(26)	0.899	0.292	0.286	‡
P(2)	0.5421(4)	0.4469(2)	0.4347(4)	†
C(2)	0.485(2)	0.526(1)	0.288(2)	†
C(31)	0.389(2)	0.448(1)	0.499(2)	4.8(3)
C(32)	0.417(2)	0.445(1)	0.669(2)	5.8(4)
C(33)	0.294(2)	0.444(1)	0.705(2)	7.3(5)
C(34)	0.151(3)	0.446(1)	0.588(3)	8.9(6)
C(35)	0.115(3)	0.449(1)	0.417(3)	8.2(6)
C(36)	0.239(3)	0.449(1)	0.374(3)	7.4(6)
C(41)	0.714(2)	0.479(1)	0.619(2)	4.2(3)
C(42)	0.784(2)	0.431(1)	0.756(2)	4.9(3)
C(43)	0.918(2)	0.451(1)	0.894(2)	5.8(4)
C(44)	0.985(2)	0.520(1)	0.896(2)	6.3(4)
C(45)	0.915(2)	0.566(1)	0.765(2)	6.4(4)
C(46)	0.779(2)	0.548(1)	0.624(2)	4.8(4)
H(32)	0.525	0.445	0.760	‡
H(33)	0.312	0.441	0.821	‡
H(34)	0.071	0.442	0.622	‡
H(35)	0.008	0.449	0.333	‡
H(36)	0.218	0.452	0.256	‡
H(42)	0.738	0.383	0.756	‡
H(43)	0.966	0.418	0.990	‡
H(44)	1.080	0.535	0.993	‡
H(45)	0.964	0.613	0.767	‡
H(46)	0.733	0.583	0.534	‡

* $B = 8\pi^2U$.

† Anisotropic thermal parameters in the form: exp-$[-2\pi^2[U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl]]$, with parameters ($\times 10^3$, for Cr and I $\times 10^4$). ‡ $B = 6.3$ (see text).

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr	352(10)	307(9)	351(9)	2(8)	183(8)	12(7)
I	561(4)	460(4)	539(4)	−21(5)	336(4)	113(5)
N	43(6)	44(6)	37(5)	−5(5)	19(5)	−6(5)
O(1)	76(8)	59(6)	59(6)	6(6)	45(6)	18(5)
C(3)	33(7)	49(8)	31(6)	1(6)	14(5)	−0(6)
O(3)	50(7)	68(7)	68(7)	3(6)	25(6)	13(6)
C(4)	38(8)	31(7)	58(8)	4(6)	22(7)	−6(6)
O(4)	44(6)	97(9)	54(6)	22(6)	17(5)	9(6)
P(1)	40(2)	28(1)	38(2)	−1(1)	19(1)	0(1)
C(1)	96(12)	29(7)	65(9)	9(8)	46(9)	16(7)
P(2)	36(2)	29(2)	33(2)	3(1)	17(1)	0(1)
C(2)	78(11)	39(8)	46(8)	14(8)	26(8)	16(7)

TABLE 3

Interatomic distances (Å) and bond angles (°)

(*a*) Distances

Cr–I	2.749(3)	Cr–P(2)	2.417(4)
Cr–N	1.705(14)	P(1)–C(1)	1.83(1)
N–O(1)	1.117(20)	P(1)–C(11)	1.86(1)
Cr–C(3)	1.883(11)	P(1)–C(21)	1.84(1)
C(3)–O(3)	1.153(15)	P(2)–C(2)	1.85(1)
Cr–C(4)	1.927(12)	P(2)–C(31)	1.84(2)
C(4)–O(4)	1.132(16)	P(2)–C(41)	1.84(1)
Cr–P(1)	2.385(4)		

(*b*) Angles

I–Cr–P(1)	86.8(1)	Cr–P(1)–C(11)	114.9(5)
I–Cr–P(2)	90.8(1)	Cr–P(1)–C(21)	114.4(4)
I–Cr–C(3)	86.3(5)	C(1)–P(1)–C(11)	104.1(6)
I–Cr–C(4)	87.2(5)	C(11)–P(1)–C(21)	103.7(7)
I–Cr–N	177.8(3)	C(1)–P(1)–C(21)	98.8(8)
N–Cr–P(1)	93.2(4)	Cr–P(2)–C(2)	110.2(6)
N–Cr–P(2)	89.2(4)	Cr–P(2)–C(31)	119.2(5)
N–Cr–C(3)	91.5(6)	Cr–P(2)–C(41)	114.9(5)
N–Cr–C(4)	95.0(6)	C(2)–P(2)–C(31)	101.0(8)
P(1)–Cr–P(2)	177.6(2)	C(31)–P(2)–C(41)	104.7(7)
C(3)–Cr–C(4)	173.5(7)	C(2)–P(2)–C(41)	105.1(7)
Cr–P(1)–C(1)	118.1(6)		

may have one of several possible identities. Of the more likely the complex could be (i) a halogenocyclohexadienyl $[Cr(CO)_2(\eta\text{-}C_6Me_6X)(NO)]$ (I), (ii) a formally seven-co-ordinate neutral species $[Cr(X)(CO)_2(\eta\text{-}C_6Me_6)(NO)]$ (II), in which the halide is metal-co-ordinated and the nitrosyl group functions as a ' bent ' one-electron donor, or (iii) a species (III) in which the arene is completely or partially cleaved from the metal. The ^1H n.m.r. spectra recorded during the reaction between $[Cr(CO)_2(\eta\text{-}C_6Me_6)(NO)]^+$ and $[PPh_4]I$ seem to rule out formation of (I), and of (II) unless the resonance due to the arene methyl protons occurs, by coincidence, at the same frequency as that for free C_6Me_6. Complexes in which partial arene displacement has occurred have been postulated as intermediates in the reactions of $[Mo(CO)_3(\eta\text{-arene})]$ with phosphines, L.[6] No n.m.r. evidence for the existence of analogues of $[Mo(CO)_3(L)(arene)]$ and $[Mo(CO)_3(L)_2(arene)]$, which contain arene ligands as four- and two-electron donors respectively, in the red solutions has been found, however, although such species may well be transient intermediates in the formation of the red products.

It therefore seems likely that arene displacement is complete in the reaction of $[Cr(CO)_2(\eta\text{-arene})(NO)]^+$ with halide ion, and that the red species must therefore be either co-ordinatively unsaturated or be stabilised by solvent, S, in a species such as *cis*-$[Cr(X)(CO)_2(S)_2(NO)]$. The second red species, formed from the first when it is set aside, also contains two carbonyl ligands, but the observation of only one i.r.-active carbonyl stretching frequency suggests it to be the *trans*-isomer of the first. The proposed *cis–trans*-isomerism undergone by the red species is similar to that observed for related complexes by Colton *et. al.*[7] Reaction of $[W(X)(CO)_4(NO)]$ with PPh_3 yields *cis*-$[W(X)(CO)_2(PPh_3)_2(NO)]$ (X = Cl, Br, or I) which on heating readily affords the *trans*-isomer. As

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[6] F. Zingales, A. Chiesa, and F. Basolo, *J. Amer. Chem. Soc.*, 1966, **88**, 2707.

[7] R. Colton and C. J. Commons, *Austral. J. Chem.*, 1973, **26**, 1487.

the analogous PPh_2Me and $PPhMe_2$ complexes did not isomerise under similar conditions, steric factors were presumed to force the *trans*-configuration only in $[W(X)(CO)_2(PPh_3)_2(NO)]$. The ease with which isomerism occurs at room temperature in the red species reported here is more likely due to the lability of the co-ordinated solvent, S, rather than to steric effects.

It is noteworthy that the carbonyl and nitrosyl stretching frequencies of the second red species, *trans*-$[Cr(X)(CO)_2(S)_2(NO)]$ are considerably higher than those of the bisphosphine derivatives *trans,trans*-$[Cr(I)(CO)_2(L)_2(NO)]$. If the proposed formulation of the red species is correct then the relative positions of the bands imply that solvent S is either a better π acceptor or a poorer σ donor than a phosphorus donor ligand. Although the former is highly unlikely, the σ-donor capacity of solvents such as ethanol or CH_2Cl_2 is certainly much lower than that of phosphines or phosphites.

The characterisation by *X*-ray diffraction studies of the phosphorus-donor ligand derivatives as *trans,trans*-$[Cr(X)(CO)_2(L)_2(NO)]$ is also of interest in the light of the ^1H n.m.r. spectrum of the iodobis(diphenylmethylphosphine) complex. The observation of an apparent doublet for the methyl resonance of the co-ordinated phosphine originally implied a *cis*-configuration for the two phosphorus ligands. The fact that the *X*-ray study revealed a *trans*-orientation suggests either that isomerisation occurs in solution or that the phosphorus–phosphorus coupling across the chromium atom is small. In view of the lack of either ^1H n.m.r. or i.r. spectral evidence for isomerisation we feel the latter is more likely.

Our structural study also allows partial confirmation of the suggested[5] geometry for *cis*-$[W(X)(CO)_2(L)_2(NO)]$. The tungsten complexes were suggested to have a *cis*-dicarbonyl, *cis*-bisphosphine structure with the nitrosyl group *trans* to X. Although the structure of *trans*-$[W(X)(CO)_2(PPh_3)_2(NO)]$ is not known, it is likely to be strictly analogous to that of *trans,trans*-$[Cr(I)(CO)_2(PPh_2Me)_2(NO)]$, *i.e.* with the nitrosyl group *trans* to X. Since isomerisation of *cis*-$[W(X)(CO)_2(PPh_3)_2(NO)]$ to the *trans*-form probably involves interchange of one carbonyl and one phosphine ligand, the suggested structure for the *cis*-isomer is likely to be correct.

The diphos complex $[Cr(I)(CO)_2(diphos)(NO)]$, which exhibits two carbonyl and one nitrosyl absorptions, almost certainly has the structure suggested by Colton for *cis*-$[W(X)(CO)_2(L)_2(NO)]$. In addition, spectral similarities between these species and $[M(X)(CO)_2(diphos)(NO)]$[8] (M = Mo or W, X = Cl, Br, or I) and $[W(X)(CO)_2(Ph_2PCH_2PPh_2)(NO)]$[9] suggest analogous structures.

EXPERIMENTAL

The preparation and purification of the complexes described were carried out under an atmosphere of dinitrogen. $[Cr(CO)_2(\eta\text{-}C_6Me_6)(NO)][PF_6]$ was prepared by the published method.[1] All solvents were dried by standard methods and deoxygenated before use.

I.r. spectra were recorded on a Perkin-Elmer PE 257 spectrophotometer; n.m.r. spectra on a Varian Associates T 60 instrument.

Dicarbonylbis(diphenylmethylphosphine)iodonitrosyl chromium, $[Cr(I)(CO)_2(PPh_2Me)_2(NO)]$.—To $[Cr(CO)_2(\eta\text{-}C_6Me_6)(NO)][PF_6]$ (1.65 g) in ethanol (20 cm^3) was added $[PPh_3Me]I$ (1.5 g). After stirring for 40 min, and filtering to remove solid $[PPh_3Me][PF_6]$, PPh_2Me (2 cm^3) was added to the red solution. The mixture was then set aside for 12 h by which time brown crystals had precipitated. Recrystallisation from dichloromethane–ethanol afforded yellow-orange crystals of the *complex* (1.1 g, 45%).

Analogous complexes of PPh_3, $PPhMe_2$, $P(OPh)_3$, and diphos were prepared similarly. They are air-stable yellow to orange solids which dissolve in polar solvents such as acetone, CH_2Cl_2, CH_3NO_2, and, to a lesser extent, ethanol, to give yellow solutions which are moderately stable in air.

Structure Determination.—The crystal of $[Cr(I)(CO)_2(PPh_2Me)_2(NO)]$ chosen for intensity measurements ($0.55 \times 0.05 \times 0.15$ mm) was mounted on a Syntex $P2_1$ four-circle diffractometer according to methods described earlier.[10] Of the total (3 079) reflections for $3.7° < 2\theta < 50°$, 2 233 were deemed ' observed ' according to the criterion $I > 2.5\sigma(I)$, and only these were used in the solution and refinement of the structure.

Crystal Data.—$C_{28}H_{26}NO_3P_2ICr$, $M = 665.5$, Monoclinic, $a = 9.796(4)$, $b = 18.019(8)$, $c = 8.968(1)$ Å, $\beta = 116.96(3)°$, $U = 1\,410.9$ Å^3, $D_c = 1.57$, $Z = 2$, $D_m = 1.56$ g cm^{-3}, $F(000) = 664$. Space group $P2_1$. Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å; $\mu(\text{Mo-}K_\alpha) = 11.12$ cm^{-1}.

The structure was solved by conventional heavy-atom methods and refined by blocked-matrix least-squares with anisotropic thermal parameters for all atoms other than those of the groups on the phosphorus atoms. Weights were applied according to the scheme: $1/w = x.y$, where $x = b/\sin\theta$ if $\sin\theta < b$, $x = 1$ if $\sin\theta > b$, and $y = F/a$ if $F > a$, $y = 1$ if $F \leqslant a$ ($a = 40.0$, $b = 0.24$).

Hydrogen atoms were at first incorporated at calculated positions but were subsequently allowed to refine isotropically. The refinement converged at R 0.055 (R' 0.068). A final electron-density difference synthesis showed no peaks >0.5 or < -0.5 eÅ^{-3}, with general background levels much lower than this. No absorption corrections were applied, and the atomic scattering factors were those of ref. 11 for non-hydrogen atoms (with correction for the real and imaginary parts of anomalous dispersion for chromium and iodine), and of ref. 12 for hydrogen. All computational work was carried out at the University of London Computing Centre with the ' *X*-Ray ' System of programmes.[13] Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21577 (13 pp., 1 microfiche).*

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

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