Alkylideneamido-derivatives of Metals and Metalloids. Part VI.[1] The Synthesis of Alkylideneamido(carbene)rhodium(I) Complexes and Related Chemistry; The Crystal and Molecular Structure of *trans*-Rh[N:C(CF$_3$)$_2$][C(NMeCH$_2$)$_2$](PPh$_3$)$_2$

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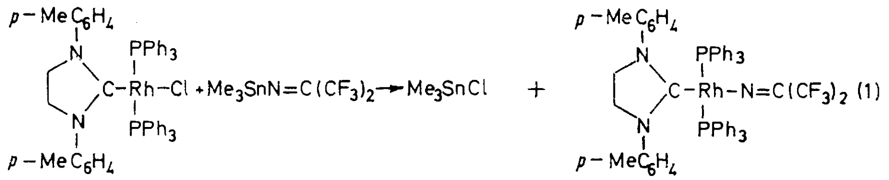
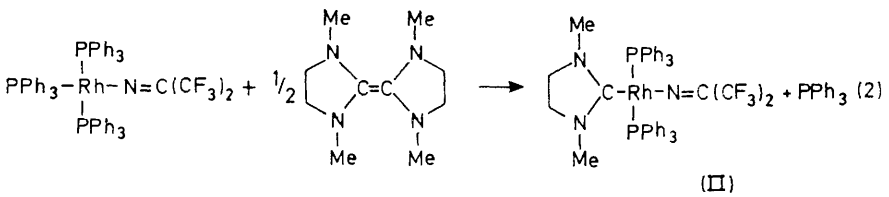
Two rhodium(I) complexes, *trans*-Rh[N:C(CF$_3$)$_2$][C(NRCH$_2$)$_2$](PPh$_3$)$_2$, (I; R = *p*-MeC$_6$H$_4$) and (II; R = Me), containing both alkylideneamido- and substituted carbene ligands have been prepared. Variable temperature ^{19}F n.m.r. spectra suggest a low barrier to planar inversion at N. It did not prove possible to rearrange these to aza-allyl/allene isomers. As a contribution to the mechanism of formation of the latter, the synthesis of a *C*-alkylideneamidocarbene complex (V) is reported. A Pt^{II} imidoyl complex Pt–C(R)=NR′, prepared by an oxidative addition reaction, did not isomerise to the alkylideneamide Pt–N=CRR′; but with HCl the former gave a 1:1 adduct, presumed to be the carbene complex Pt–C(R)NHR′. A single crystal *X*-ray analysis of (II) has been carried out to *R* 0·067 for 2853 independent terms: the complex has an approximately square planar Rh environment with disorder about N:C and Rh–N, 2·02(3); N=C, 1·27(3); Rh–P, 2·290(4) and 2·291(4); and Rh–C$_{carb}$, 2·006(15) Å, and RhNC = 152°. Noteworthy are the significant departure from linearity at N and the exceptionally short mutually *trans*-Rh–P bond lengths; the M–NO/M–N:NR analogy is extended to M–N:CR$_2$.

THIS paper relates to our studies not only on alkylideneamido-complexes of the type LM–N=CR$_2$ (where L represents all ligands other than the alkylideneamido-groups attached to the Main Group or transition metal atom M),[1] but also to transition metal carbene complexes LM–CXY.[2] Here we report the preparation, spectroscopic properties, and, in one case also the crystal and molecular structure, of two novel rhodium complexes which contain both these functional groups, and some loosely related chemistry, including a chromium(0) *C*-alkylideneamidocarbene complex Cr(CO)$_5$[C(OEt)-NCPh$_2$], a Pt^{II} imidoyl species *cis*-Pt[C(:NMe)Ph]Cl-(PPh$_3$)$_2$, and a carbene complex derived therefrom, *cis*-[PtCl{C(NHMe)Ph}(PPh$_3$)$_2$]Cl.

The routes to the two new Rh^I compounds are shown in equations (1) and (2). Compounds such as (I) and (II) are of interest *inter alia* because of the possibility of realising reactions which involve interaction between the carbene ligand and either the M–N or C=N bonds of the alkylideneamido-group. This latter aspect relates to the report of Kilner that MoCl(π-C$_5$H$_5$)(CO)$_3$ reacts with LiN=CPh$_2$ to give mainly Mo(π-C$_5$H$_5$)(CO)$_2$[Ph$_2$CNCPh$_2$], (IV).[3] In this unusual reaction LiNCO was also detected in the reaction mixture; it is possible that the reaction pathway involves a reactive diphenylcarbene–alkylideneamido-intermediate, (III) [equation (3)].[4] [Subsequent *X*-ray structure studies of (IV) confirmed it to have an aza-allene, rather than an aza-allyl structure.[5]] In support of this reaction sequence, we find that a Group VIA carbonyl reacts with LiN=CPh$_2$ without loss of LiNCO to give a lithio-derivative which was readily converted into the red ethoxycarbene complex (V), using triethyloxonium tetrafluoroborate [*cf.*,[6] the similar reaction between Cr(CO)$_6$ and LiNEt$_2$, equation (4)]. Hence step (3a) and (III) are authenticated by analogy. Compounds (I) and (II) are generically related to (III), but their conversion (3c) into an analogue of (IV) was not achieved. An attempt to prepare a related Cr^0 carbene complex from Cr(CO)$_6$ and Me$_3$SiN:CPh$_2$ or Me$_3$SnN:C(CF$_3$)$_2$ was unsuccessful.



(I)



(II)

The reaction between rhodium alkylideneamides of the type Rh(N=CR$_2$)(PPh$_3$)$_3$ and diphenyldiazomethane

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[1] Part V, B. Cetinkaya, M. F. Lappert, and J. McMeeking, *J.C.S. Dalton*, 1973, 1975.

[2] B. Cetinkaya, P. Dixneuf, and M. F. Lappert, *J.C.S. Dalton*, 1974, in the press and earlier papers in that series.

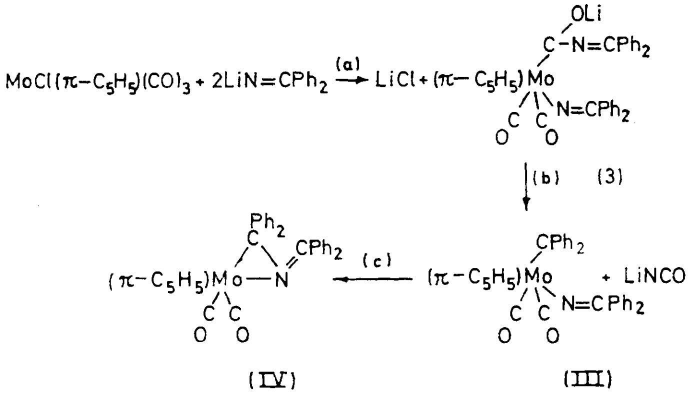
[3] K. Farmery, M. Kilner, and C. Midcalf, *J. Chem. Soc.* (*A*), 1970. 2279.

[4] H. R. Keable and M. Kilner, *J.C.S. Dalton*, 1972, 153; J. McMeeking, M.Sc. Thesis, University of Sussex, 1969.

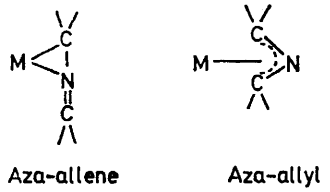
[5] H. M. M. Shearer and J. D. Sowerby, unpublished work, cited in ref. 4.

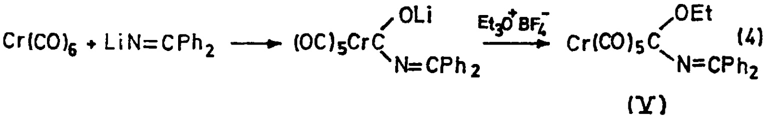
[6] E. O. Fischer and H. J. Kollmeier, *Angew. Chem. Internat. Edn.*, 1970, **9**, 309.

might reasonably be expected to give (with loss of nitrogen) related rhodium aza-allyl/allene complexes. There are, as yet few analogous Rh^I allyls,[7a] although a simple complex has been reported.[7b] Thermal (rather than photolytic) reactions of Ph_2CN_2 do not in general lead to diphenylcarbene derivatives but recently the thermal reaction between Ph_2CN_2 and $RhCl(PPh_3)_3$ has been reported to yield a number of such carbene complexes.[8] Unfortunately, neither $Rh(N{=}CPh_2)(PPh_3)_3$ nor $Rh[N{=}C(p\text{-}MeC_6H_4)_2](PPh_3)_3$ were available for use in our reactions, because their attempted preparation from $RhCl(PPh_3)_3$ by the lithium chloride or trimethyltin chloride elimination routes led, in each case, to the products of decomposition.[1] The instability of the desired complexes may be associated with their tendency to undergo loss of $HN{=}CR_2$ in a manner which parallels the behaviour of $RhMe(PPh_3)_3$.[9] Consequently the more thermally stable, readily prepared, although less suitable $Rh[N{=}C(CF_3)_2](PPh_3)_3$ was used. There was no reaction between this rhodium compound and Ph_2CN_2 in benzene during 8 h at room temperature, but during a further 24 h at 70° the diphenyldiazomethane was consumed, presumably[10] to give benzophenone azine because there was no evidence (i.r., analysis) to suggest its incorporation, or that of Ph_2C, on to rhodium. The starting rhodium complex itself decomposed to give a compound which was also obtained in the absence of added diphenyldiazomethane.



An alternative route to rhodium aza-allyl/allene complexes was also explored [equation (1)]. Under the conditions of reaction (1 h, reflux) a compound identified as (I) (see Table 1) was obtained in preference to the possible rearrangement product. Additionally, the mass spectrum showed no peaks attributable to an aza-allene group. The reaction between $RhN{=}C(CF_3)_2(PPh_3)_3$ and an electron-rich olefin [equation (2)] gave a similar product (II). As with the trimethyltin chloride route,





$$\mathrm{Cr(CO)_6 + LiN{=}CPh_2 \longrightarrow (OC)_5CrC}\genfrac{}{}{0pt}{}{\diagup \mathrm{OLi}}{\diagdown \mathrm{N{=}CPh_2}} \xrightarrow{\mathrm{Et_3O^+BF_4^-}} \mathrm{Cr(CO)_5C}\genfrac{}{}{0pt}{}{\diagup \mathrm{OEt}}{\diagdown \mathrm{N{=}CPh_2}} \quad (4)$$

(V)

TABLE 1

Selected data on new alkylideneamido-complexes

Complex	Analyses (%) Found (Required) C	H	N	^{1}H N.m.r. (τ)[a] $-CH_2-CH_2-$	N–()–CH_3	^{19}F N.m.r.[b] (t/°C)		M.p. (t/°C)
$Rh[N{=}C(CF_3)_2]L^{Tol}(PPh_3)_2$ (I)	63·4 (64·6)	4·8 (4·6)	3·9 (4·0)	7·29s	7·73s	+68·53 (t) $J(^{31}P-^{19}F)$ 2·0 Hz +68·5 (bs)	+80 +25	205—212 (dec.)
$Rh[N{=}C(CF_3)_2]L^{Me}(PPh_3)_2$ (II)	58·8 (59·4)	4·6 (4·5)	4·8 (4·7)	7·75s	7·05s	+68·68 (t) $J(^{31}P-^{19}F)$ 2·0 Hz +68·6 (bs)	+25 −80	141—143 (dec.)

[a] C_6H_6 solvent. [b] C_7D_8 solvent; δ in p.p.m. relative to $CFCl_3$. (t) triplet, (s) singlet, (bs) broad singlet.

I.r. Spectra (Nujol, cm^{-1})

(I): 3065w, 3040w, 1670vw, 1583w, 1570w, 1555vw, 1508m, sh, 1500m, 1280ms, 1230mw, 1212m, 1192vs, 1159mw, 1130s, 1113ms, 1090ms, 1085ms, sh, 1068m, 1028w, 1000w, 921ms, 751ms, 742ms, 700vs, 696m, sh, 670w, 643w, 520vs, 512s, 505s, 491m, 455w, 433w, 415m, 400w, sh. No peaks 400—250 cm^{-1}.

(II): 3060w, 3022mw, 1580w, 1569w, 1555vw, sh, 1505m, (1385ms?), 1312m, 1285m, sh, 1271s, 1243m, 1227w, 1211m, 1190vs, 1137s, 1110m, sh, 1089ms, 1040w, 1025w, 997w, 950w, 914m, 843vw, 811s, 755ms, 749s, 743s, 724w, 695vs, 670ms, 648ms, 620w, 573vs, 545w, 510s, sh, 490m, 452m, 432w, 415m, 385m, sh.

[7] (a) S. O'Brien, *Chem. Comm.*, 1968, 757; (b) T. Kashiwagi, N. Yasuoka, N. Kasai, and M. Kukudo, *Chem. Comm.*, 1969, 317.

[8] P. Hong, N. Nishii, K. Sonogashira, and N. Hagihara, *J.C.S. Chem. Comm.*, 1972, 993.

[9] W. Keim, *J. Organometallic Chem.*, 1968, **14**, 179.

[10] *Cf.* D. Bethell, D. Whittaker, and J. D. Callister, *J. Chem. Soc.*, 1965, 2466.

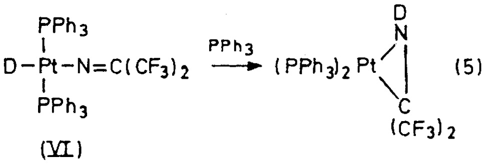
the resultant complexes appear (see Table 1) to contain discrete and independent carbene and alkylideneamido-ligands, although an unambiguous structural assignment depends on the *X*-ray analysis described below.

Rhodium complexes of the type

$$\mathrm{RhX(\overline{C{\cdot}NR{\cdot}CH_2{\cdot}CH_2N}R)(PPh_3)_2}$$

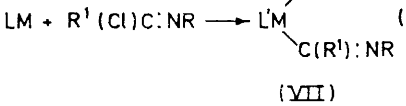
(X = Cl, Br, I) are known from earlier work in our laboratory.[11] These compounds, despite their low solubility in solvents such as xylene and benzene, are active catalysts for electron-rich olefin metatheses;[12] a result which implies some lability of the carbene fragment. The alkylideneamido-group in the two novel rhodium complexes confers increased solubility in these solvents, and also enhanced air-stability in solution.

It is not yet clear which factors control carbene lability on a transition metal.[11] In the molybdenum case,[3] the diphenylcarbene ligand would be expected to be considerably more electrophilic, and the nitrogen atom of the alkylideneamido-group somewhat more nucleophilic, than in the rhodium complex, thus favouring ligand migration only for the former. However, steric factors may be important. We have reported the phosphine catalysed tautomeric hydrogen transfer from platinum to the $-N{=}C(CF_3)_2$ ligand [equation (5)]. Under similar conditions, methyl and phenyl groups show no tendency to migrate. For reaction (5), it is probable that a necessary intermediate is the *cis*-isomer of (VI). The difficulty of formation of the *cis*-isomer of (I) may be the reason for its reluctance to undergo tautomerism.



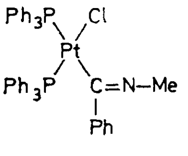
(VI)

Metal alkylideneamides, $LM{-}N{=}CR_2$, are isomeric with imidoyl complexes $LM{-}C(R){=}NR$. We were interested in the possible interconversion of the two forms (*cf.* the Beckmann Rearrangement). A novel procedure was used for the preparation of the latter—the oxidative addition reaction of an imidoyl halide to a low-valent transition metal compound [equation (6)]. Such a reaction has been explored previously with LM a Rh^I complex.[13] Although an intermediate such as (VII) was postulated, the isolated product was a Rh^{III} carbene complex $Rh^{III}{-}C(R')NRC(R'){=}NR$ [13] or $Rh^{III}{-}C(R')$-NHR.[14] Platinum imidoyl complexes had already been prepared by insertion of isocyanides into platinum–carbon bonds.[15]

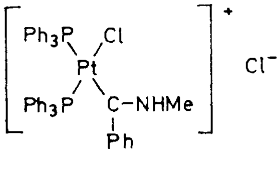


(VII)

The reaction between *N*-methylbenzimidoyl chloride and tetrakis(triphenylphosphine)platinum(0) gave three main products: *cis*-dichlorobis(triphenylphosphine)-platinum(II); the expected imidoyl complex (VIII);[15] and a third, as yet unidentified product. The separation and purification of the products proved to be extremely difficult. Compound (VIII) readily formed a 1 : 1 adduct with hydrogen chloride, which is probably the carbene complex (IX), partly on the basis of prior art.[14] There was no evidence for the formation of platinum alkylideneamides during these reactions.



(VIII)



(IX)

CRYSTALLOGRAPHIC STUDIES

Crystal Data.—$C_{44}H_{40}F_6N_3P_2Rh$, $M = 889{\cdot}3$, Monoclinic, $a = 20{\cdot}228(4)$, $b = 20{\cdot}714(4)$, $c = 9{\cdot}836(2)$ Å, $\beta = 96{\cdot}08(7)°$, $U = 4098{\cdot}1$ Å^3, $D_m = 1{\cdot}48$, $Z = 4$, $D_c = 1{\cdot}44$, $F(000) = 1816$, space group $P2_1/n(C_{2h}^5)$ [16] from systematic absences: $h0l$ for $h + l = 2n + 1$, and $0k0$ for $k = 2n + 1$. Mo-K_α radiation (graphite crystal monochromator), $\lambda = 0{\cdot}70926$ Å, μ(Mo-K_α) = $5{\cdot}52$ cm^{-1}.

Preliminary values of the cell dimensions were obtained from precession photographs and were subsequently adjusted by least-squares refinement of the setting angles of twelve reflections measured on a Hilger and Watts Y290 four circle diffractometer using Mo-K_α radiation with a graphite crystal monochromator. The data crystal was a small orange coloured parallelipiped of dimensions 0·34 × 0·22 × 0·18 mm. Intensity data were collected by the $\theta - 2\theta$ scan step procedure, each reflection being scanned in 50 one second steps of 0·01° from 0·25° below to 0·25° above $2\theta_{calc}$. Stationary background counts were measured for 25 s at each end of the scan range. The intensities of three standard reflections were monitored periodically to check crystal and electronic stability. Intensities were collected for reflections with $\theta(\text{Mo-}K_\alpha) \leqslant 22°$, and 2853 reflections for which $I \geqslant 3\sigma(I)[\sigma(I) = \{\text{total peak intensity} + \text{total background intensity} + (0{\cdot}04I)^2\}^{\frac{1}{2}}]$ were accepted as being significantly above background. These were corrected for Lorentz and polarisation effects, but not for absorption.

Structure Analysis.—Approximate co-ordinates of the Rh atom were derived from a 3-dimensional Patterson synthesis. A structure factor calculation based on this gave *R* 0·36. The co-ordinates of the remainder of the

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[11] *Cf.* D. J. Cardin, B. Cetinkaya, M. J. Doyle, and M. F. Lappert, *Chem. Soc. Rev.*, 1973, **2**, 99.

[12] D. J. Cardin, M. J. Doyle, and M. F. Lappert, *J.C.S. Chem. Comm.*, 1972, 927.

[13] P. B. Hitchcock, M. F. Lappert, G. M. McLaughlin, and A. J. Oliver, *J.C.S. Dalton*, 1974, 68.

[14] M. F. Lappert and A. J. Oliver, *J.C.S. Dalton*, 1974, 65.

[15] P. M. Treichel and R. W. Hess, *J. Amer. Chem. Soc.*, 1970, **92**, 4731; Y. Yamamoto and H. Yamazaki, *Bull. Chem. Soc. Japan*, 1970, **43**, 3634.

[16] A non-standard form of the space group $P2_1/c$ No. 14, International Tables for *X*-ray Crystallography, vol. 1, Kynoch Press, Birmingham, 1962.

atoms were derived from subsequent electron density distributions. Least-squares refinement of positional and isotropic thermal parameters, using the programme CRYLSQ in the blocked mode,[17] gave R 0·091. The function minimised was $\Sigma\omega(|F_o| - |F_c|)^2$, where $\omega = 1/\sigma^2(F^2)$. Scattering factors were taken from ref. 18, except those for hydrogen.[19] Anomalous dispersion was accounted for by using Comer's [20] values of $\Delta f'$ and

TABLE 2(a)

Final fractional co-ordinates ($\times 10^4$) and isotropic thermal parameters (Å $\times$ 10^3, the numbering refers to Figure 1)

	x	y	z	U
Rh	8069(0)	2352(0)	725(1)	*
P(1)	8367(2)	3284(2)	−301(3)	*
P(2)	7806(2)	1422(2)	1806(3)	*
F(1)	9431(7)	561(5)	−836(14)	*
F(2)	8657(8)	1150(8)	−1816(22)	*
F(3)	9664(9)	1255(6)	−2193(12)	*
F(4)	10400(6)	1268(7)	488(20)	*
F(5)	10321(7)	2155(11)	−342(23)	*
F(6)	10092(12)	2052(9)	1546(19)	*
N(1)	7257(6)	3114(5)	2518(12)	*
N(2)	6664(5)	2817(6)	572(15)	*
C(1)	7251(7)	2785(6)	1271(14)	*
C(2)	6573(11)	3346(10)	2631(30)	*
C(3)	6173(8)	3199(10)	1296(25)	*
C(4)	7788(9)	3136(8)	3593(15)	*
C(5)	6492(8)	2561(10)	−787(18)	*
C(6)	9338(8)	1663(8)	−136(19)	*
C(7)	9283(9)	1148(10)	−1259(22)	*
C(8)	10038(11)	1763(9)	424(22)	*
N(3a)	8718(12)	1836(11)	−247(25)	73(7)
N(3b)	8999(9)	2027(8)	568(18)	36(5)
C(9)	7676(6)	3828(6)	−969(13)	54(3)
C(10)	7460(8)	3802(7)	−2383(17)	84(5)
C(11)	6885(9)	4205(9)	−2841(19)	112(6)
C(12)	6595(9)	4569(9)	−1929(20)	109(6)
C(13)	6800(8)	4600(8)	−589(19)	99(5)
C(14)	7367(7)	4210(7)	−61(15)	76(4)
C(15)	8830(6)	3186(6)	−1797(12)	55(3)
C(16)	8631(7)	2698(8)	−2682(16)	86(4)
C(17)	8972(9)	2582(8)	−3853(18)	103(5)
C(18)	9487(8)	2989(8)	−4105(17)	93(5)
C(19)	9699(8)	3464(8)	−3234(16)	83(5)
C(20)	9369(7)	3588(7)	−2037(14)	70(4)
C(21)	8927(6)	3827(6)	768(13)	54(3)
C(22)	9354(7)	3539(7)	1761(15)	72(4)
C(23)	9848(8)	3929(8)	2531(16)	84(5)
C(24)	9852(8)	4605(8)	2304(16)	88(5)
C(25)	9407(8)	4877(8)	1326(16)	84(5)
C(26)	8927(7)	4507(7)	498(14)	71(4)
C(27)	8532(6)	954(6)	2415(12)	51(3)
C(28)	9014(7)	1267(7)	3274(15)	77(4)
C(29)	9632(9)	900(9)	3779(17)	100(5)
C(30)	9685(9)	282(9)	3345(18)	98(5)
C(31)	9234(9)	−20(8)	2429(18)	98(5)
C(32)	8621(7)	319(7)	1974(15)	75(4)
C(33)	7341(6)	1486(6)	3316(13)	53(3)
C(34)	6672(6)	1671(6)	3066(13)	59(4)
C(35)	6280(7)	1726(7)	4180(16)	80(4)
C(36)	6591(9)	1627(9)	5513(19)	103(6)
C(37)	7242(9)	1443(9)	5750(18)	106(6)
C(38)	7636(7)	1358(7)	4623(15)	73(4)
C(39)	7289(5)	836(5)	812(12)	43(3)
C(40)	7260(7)	858(7)	−596(15)	78(4)
C(41)	6876(9)	362(9)	−1394(19)	109(6)
C(42)	6547(8)	−104(8)	−742(18)	94(5)
C(43)	6578(8)	−127(7)	630(17)	82(5)
C(44)	6949(7)	344(7)	1485(14)	73(4)

* These atoms were refined anisotropically.

TABLE 2(b)

Thermal parameters (Å $\times$ 10^3) of atoms refined anisotropically expressed in the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ (for atom numbering, see Figure 1)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	38(1)	36(1)	47(1)	0(1)	10(0)	0(1)
P(1)	44(2)	39(2)	49(1)	−2(2)	7(2)	3(2)
P(2)	40(2)	40(2)	41(2)	0(2)	5(2)	0(2)
F(1)	231(14)	83(8)	193(12)	25(8)	25(11)	−11(8)
F(2)	176(15)	188(15)	403(26)	−28(12)	−88(17)	−24(16)
F(3)	317(20)	151(11)	107(9)	69(11)	63(11)	−5(8)
F(4)	108(10)	194(14)	360(22)	29(10)	−68(12)	−27(16)
F(5)	146(13)	378(28)	362(26)	−143(16)	1(14)	158(22)
F(6)	410(29)	214(18)	228(18)	−94(19)	−2(19)	−101(15)
N(1)	103(10)	54(8)	102(9)	28(7)	51(8)	8(7)
N(2)	45(7)	89(10)	183(14)	16(7)	18(8)	63(10)
C(1)	81(10)	42(9)	79(10)	6(7)	33(8)	13(7)
C(2)	117(19)	91(15)	278(31)	47(14)	140(20)	12(19)
C(3)	51(12)	117(17)	197(24)	35(11)	48(13)	46(17)
C(4)	139(15)	100(13)	60(10)	−4(11)	8(10)	−16(9)
C(5)	83(12)	153(18)	124(15)	−32(12)	−41(11)	25(13)
C(6)	61(11)	61(10)	143(16)	10(4)	47(11)	42(11)
C(7)	99(15)	113(17)	157(20)	5(12)	−12(13)	−13(15)
C(8)	138(19)	110(16)	177(21)	−39(14)	67(17)	−9(14)

TABLE 3

(a) Bond lengths (Å), excluding those involving N(3) (for atom numbering, see Figure 1)

Rh–P(1)	2·290(4)	P–C_{Ph}	1·836(6) [a]
Rh–P(2)	2·291(4)	F–C	1·284(15) [a]
Rh–C(1)	2·006(15)	C_{Ph}–C_{Ph}	1·404(5) [b]
N(1)–C(1)	1·402(18)	N(2)–C(1)	1·308(17)
N(1)–C(2)	1·480(26)	N(2)–C(3)	1·507(25)
N(1)–C(4)	1·424(19)	N(2)–C(5)	1·446(23)
C(2)–C(3)	1·498(35)	C(6)–C(7)	1·531(27)
		C(6)–C(8)	1·479(27)

(b) Bond angles (°), excluding those involving N(3)

P(1)–Rh–P(2)	178·0(1)	Rh–C(1)–N(1)	121·4(9)
P(1)–Rh–C(1)	90·3(4)	Rh–C(1)–N(2)	127·6(10)
P(2)–Rh–C(1)	90·7(4)	N(1)–C(1)–N(2)	110·9(12)
Rh–P–C_{Ph}	116·1(2) [a]	N(1)–C(2)–C(3)	106·9(20)
C_{Ph}–P–C_{Ph}	102·1(3) [a]	N(2)–C(3)–C(2)	101·5(15)
C(1)–N(1)–C(2)	107·6(14)	C(7)–C(6)–C(8)	111·0(15)
C(1)–N(1)–C(4)	126·9(12)	F–C–F	106·5(10) [a]
C(2)–N(1)–C(4)	124·7(16)	C–C–F	112·2(9) [a]
C(1)–N(2)–C(3)	112·7(14)	P–C_{Ph}–C_{Ph}	118·9(5) [a]
C(1)–N(2)–C(5)	125·6(13)	C_{Ph}–C_{Ph}–C_{Ph}	120·0(4) [b]
C(3)–N(2)–C(5)	121·6(13)		

[a] Mean of 6 independent values. [b] Mean of 36 independent values.

TABLE 4

Geometry around N(3) (for atom numbering, see Figure 1)

	Model 1 (refined) high anisotropy	Model 2 (refined) N(3) only disordered	Model 3 (calculated) N(3) and C(6) disordered
Rh–N(3)	1·966(17)	2·013(26) 2·020(20)	2·02 Å
N(3)–C(6)	1·179(24)	1·297(28) 1·272(25)	1·27 Å
Rh–N(3)–C(6)	172·4(15)	141·3(18) 143·1(14)	152°
P(1)–Rh–N(3)	89·2(5)	91·3(7) 87·5(5)	89°
P(2)–Rh–N(3)	89·8(5)	88·3(7) 91·2(5)	90°
N(3)–Rh–C(1)	177·9(7)	164·5(7) 166·4(6)	165°
N(3)–C(6)–C(7)	126·2(16)	97·9(16) 143·5(16)	120°
N(3)–C(6)–C(8)	122·6(16)	150·7(19) 105·3(16)	120°

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TABLE 5

Least-squares planes, expressed in the form $Pz + Qy + Rz = S$, with displacements (Å) of atoms from these planes. σ Is the mean standard deviation of the atoms defining the plane from the plane (for atom numbering, see Figure 1)

Plane (*a*): Rh, N(1), N(2), C(1), C(2), C(3)

Rh −0·005, N(1) 0·034, N(2) −0·013, C(1) −0·003, C(2) −0·042, C(3) 0·029, C(4) −0·060, C(5) 0·020

Plane (*b*): Rh, N(3a), N(3b), C(6), C(7), C(8)

Rh −0·020, N(3a) 0·101, N(3b) −0·059, C(6) −0·004, C(7) −0·041, C(8) 0·023

Plane (*c*): Rh, P(1), P(2), N(3a), N(3b), C(1)

Rh −0·005, P(1) 0·018, P(2) 0·045, N(3a) −0·518, N(3b) 0·487, C(1) −0·027

	P	Q	R	S	σ
(*a*)	6·389	17·673	−4·393	9·000	0·028
(*b*)	3·667	14·954	−6·722	6·009	0·057
(*c*)	8·757	6·121	7·870	9·083	0·319

Angles between the planes: (*a*)—(*b*) 18·1°, (*a*)—(*c*) 88·0°, (*b*)—(*c*) 73·9°

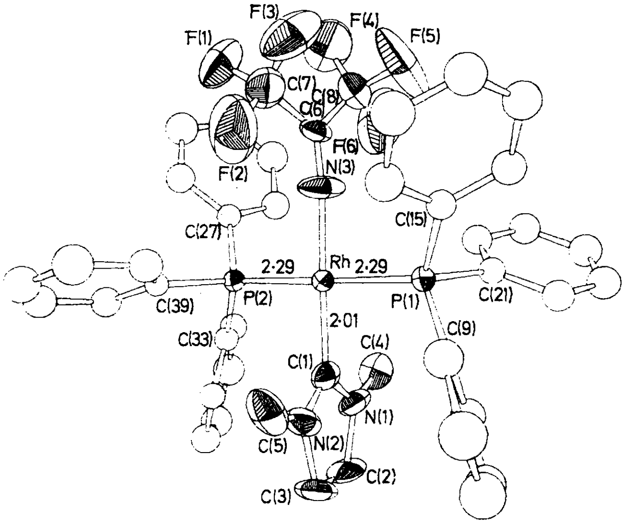

FIGURE 1 View of the molecule showing the numbering system used and thermal motion of atoms refined anisotropically (30% probability ellipsoids)

$\Delta f''$ for rhodium and phosphorus. A difference synthesis calculated at this point indicated anisotropic motion of the rhodium and fluorine atoms. Allowance was therefore made for anisotropic vibration of rhodium, the 2 phosphorus atoms and the 2 CF_3 groups which upon refinement reduced R to 0·076. The resulting difference map indicated anisotropic thermal vibration in both carbene and ketimide ligands especially atom N(3); after acounting for this, further refinement converged at R 0·067. However, because of the high anisotropy of N(3) [U_{11} 0·16, U_{22} 0·10, U_{33} 0·29, U_{12} 0·08, U_{13} 0·18, U_{23} 0·11] and the short Rh–N(3) and N(3)–C(6) bond lengths (Table 4, model 1), this atom was removed and after another cycle of refinement a further difference map with a grid resolution of 0·25 Å was calculated. This clearly showed 2 maxima in the elongated peak separated by *ca.* 1 Å. A '½ nitrogen atom' was attributed to each maximum and further refinement again converged at R 0·067. This model gave chemically more reasonable bond lengths and a bent Rh–N(3)–C angle of 141°, but yielded unfavourable N(3)–C(6)–C angles (Table 4, model 2). An unsuccessful attempt was made to resolve disorder in C(6), but separating '½ atom centres' by only 0·5 Å along the principal axis of thermal vibration yielded satisfactory geometry (Table 4, model

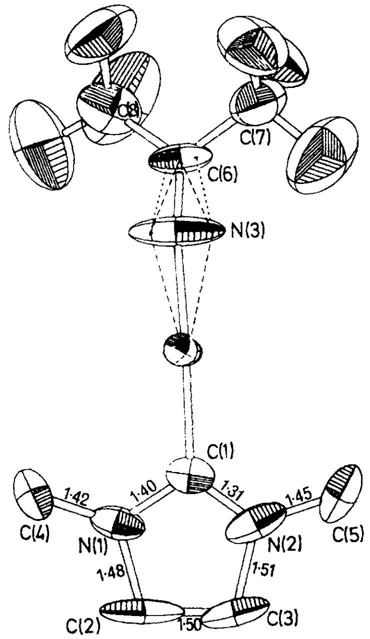

FIGURE 2 View of the P–Rh–P bonds showing the geometry of the carbene ligand and the disordered models for the ketimido-ligand. Model 1 (normal), model 2 (long broken lines), and model 3 (long and short broken lines)

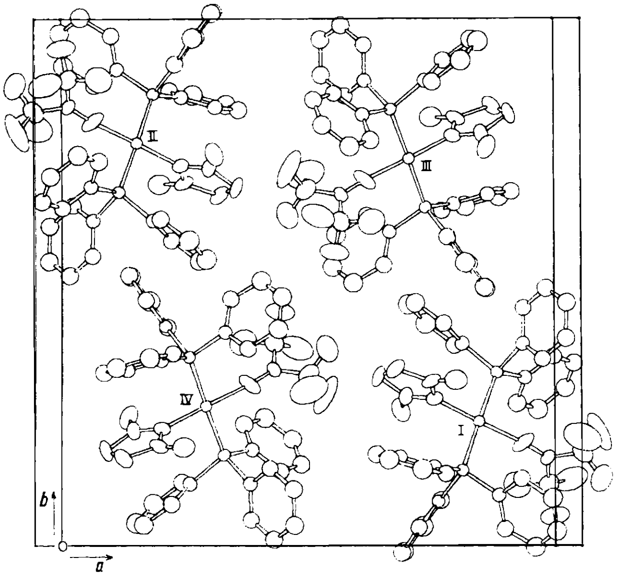

FIGURE 3 Unit cell contents viewed down C^*. I corresponds to the final co-ordinates of the molecule as listed in Table 1. II is related to I by a centre of symmetry at the centre of the cell. III is related to I by the symmetry operation $\frac{1}{2} - x + 1$, $\frac{1}{2} + y$, $\frac{1}{2} - z$ and IV is related to III again by a centre of symmetry at the centre of the cell

3). Hydrogen atom positions were not clearly distinguishable above the general background of $\pm 0{\cdot}4\,e$ in the final difference map and therefore were not included in any subsequent calculation. During the final cycle of refinement all variable parameter shifts were $< 0{\cdot}4\sigma$ and the adequacy of the weighting scheme was indicated by a subsequent analysis of $\omega(|F_o| - |F_c|)^2$ against F_o and $\sin\theta/\lambda$ which showed no systematic trends.

Both the weighted and normal discrepancy indices of the ordered (model 1) and disordered (model 2) structures were the same. The atomic parameters [excluding N(3)] were within 2σ as were bond lengths and angles. The values referred to in Tables 2, 3, and 5 are for model 2, as is the listing of observed and calculated structure factors available in Supplementary Publication No. SUP 20978 (4 pp.).*

Results and Discussion of Structure.—The structural features of interest for metal alkylideneamides centre on (i) the state of molecular aggregation and (ii) the angle at N.[21] In terms of the monomer, the possibility of association arises because of the presence of potential donor (the N-atom, with a lone pair of electrons) and acceptor (the metal) sites; accordingly, the alkylideneamido-ligand in various complexes is known both as a terminal and a bridging (for dimers) moiety. Terminal metal dialkylamides $L_nM{-}\dot{N}R_2$ are invariably found with approximately trigonal environment around N, corresponding to sp^2-hybridisation at N possibly because of $Np_z \longrightarrow M$ π-bonding. It might therefore be expected that terminal alkylideneamides will approximate to a linear arrangement at (sp)N, unless $N \longrightarrow M$ π-bonding is precluded. In solution, alkylideneamides are bent at N, with a high barrier to planar inversion at N (*ca*. 30 kcal mol^{-1}) which, however, is appreciably lowered by an electronegative substituent in place of H [*viz*.,[22] 9·2 kcal mol^{-1} in $Me_3GeN{=}C(Ph)C_6H_4{\cdot}CF_3\text{-}p$]. A low barrier to planar inversion at N is suggested by the ^{19}F n.m.r. spectrum of (II). At 25 °C, in deuteriotoluene, a well resolved triplet is observed (Table 1) indicating the two trifluoromethyl groups to be equivalent, and coupled to two equivalent ^{31}P nuclei. The triplet collapses on cooling to −60 °C and at −80 °C only a broad singlet is observed. Separate signals, however, due to *syn*- and *anti*-trifluoromethyl groups, would be expected if inversion at N was ' frozen out ' at this temperature. The broadening may be due to a slowing down of inversion at N; however, a decrease in the rate of rotation about the Rh–N bond, even with rapid inversion would be expected to give the same effect. It is noteworthy that the variable-temperature ^{19}F n.m.r. spectrum of (II) differs from that of (I) in which the N-substituent on the carbene ligand is the more bulky *p*-tolyl group. At 25° a broad singlet is observed, which with increasing temperature gives the expected well resolved triplet. The change in bulk of the N-substituent would be expected *inter alia* to change the rotational properties of the carbene ligand about the Rh–C$_{carb}$ bond, and in this way, therefore, may also influence the profile of the variable-temperature ^{19}F spectra to some extent. The alkylideneamido- ($R_2C{=}N{-}$) and alkyldiazo- ($R{-}N{=}N{-}$) ligands are electronically related. The latter ligand is presumably capable of acting as a three-electron donor in $(CO)_2CpMo\overset{\curvearrowleft}{-}\ddot{N}{=}NCH_2SiMe_3$ [23a] in order to give Mo the favourable 18-electron count, or a one-electron donor in *trans*-$Cl(Et_3P)_2Pt{-}N{=}NAr$,[23b] a d^8 metal complex for which a 16-electron count is usual. The Mo complex might therefore be expected to have the angle MNN more nearly linear than the Pt species; examples of linear [*e.g.*,[24a] $Re^{III}Cl_2(N_2Ph)(PMe_2Ph)_3$] and bent,[24b] $[RhCl(N_2Ph)\{Ph_2P(CH_2)_3PPh_2\}]^+PF_6^-$, $PhN{\vdots}N{-}$ ligands are known. A similar correlation of angle at N with bonding is, of course, best established for the metal nitrosyls.[24c]

There are very few *X*-ray determinations of metal alkylideneamide structures.[25] Data ($M\widehat{N}C$ bond angles in parentheses) relate to $(1,3,5\text{-}Me_3C_6H_2)_2BN{=}CPh_2$ [173(2)^0],[26] $LiAl(N{=}CBu^t_2)_4$ (167·2°),[27] $[Me_2AlN{=}C(Me)Bu^t]_2$,[28] $[Ph_2AlN{=}C(Ph)C_6H_4{\cdot}Br\text{-}p]_2$,[29] $(OC)_2(cp)MoN{=}CBu^t_2$(172°),[30] $[(OC)_3FeN{=}C(C_6H_4Me\text{-}p)_2]_2$,[31] and $(OC)_3\text{-}FeN{=}C(Ph)CH{=}C(Ph)CH_2C(Ph){=}NFe(CO)_3$.[32] Although useful information was obtained in the present investigation, it is unfortunate that the disorder problem described above, involving N(3) and C(6), provides a limitation on detailed discussion.

The plane of the alkylideneamido-ligand makes a dihedral angle of 73·9° with the co-ordination plane of the rhodium (Table 5). The Rh–N(3)–C(6) angle of 152° (Table 4, model 3) is significantly bent, in marked contrast to the almost linear value of 172° for the Mo–N–C angle in $(OC)_2(\pi\text{-}C_5H_5)MoN{=}C(Bu^t)_2$,[30] which is similar to the value of 172·4° for model 1.

The Rh–N(3) distance of 2·02(2) Å is *ca*. 0·1 Å shorter than the essentially single bond $Rh^I{-}N$ sp^2 value of

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue. Items less than 10 pp. are sent as full-size copies.

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2·127(7) Å in $RhCl(CO)_2$(diazepine).[33] The N(3)–C(6) bond length of 1·27(3) Å has the same value as in $(OC)_2(cp)MoN{=}C(Bu^t)_2$ [30] and is comparable with double bonds in organic compounds [*e.g.*, 1·284(5) Å in glyoxime [34]]. As with other structures containing $-CF_3$ groups (*e.g.*, ref. 35), these appear to suffer from slight disorder which is reflected in the high anisotropic thermal parameters. However, the average bond lengths and angles quoted in Table 3 are close to accepted values.

The mutually *trans*-Rh–P distances of 2·290(4) and 2·291(4) Å are unusually short (see Table 6): it will be seen that for the two compounds with closest Rh–P distances to those now reported, $[(diphos)_2Rh]^+ClO_4^-$ and $(PBu^tPr^n{}_2)_2RhHCl_2$, there are clear reasons (cation, chelate effect, bulky ligand, high oxidation state) for short bonds. Structurally related complexes show substantially longer mutually *trans*-Rh^I–P distances of 2·335(2) and 2·337(2) Å in $(PPh_3)_2Rh(CS)Cl$ [36] and 2·327(8) and 2·315(8) Å in $(PPh_3)_3RhCl$ [37]. Mutually *trans*-Rh–P distances fall within the range 2·31—2·40 Å [36-45] irrespective of the oxidation state or geometry of the rhodium. Remarkably, the octahedral Rh^{III}–P bond [2·368(3)—2·400(5) Å] [40,41] seems significantly longer than the square planar Rh^I–P bond [2·290(4)—2·337(2) Å] (see also this work),[36,45] contrary to expectation; the estimated radius of Rh^I (1·407 Å[33]) is greater than that of Rh^{III} (1·34 Å [46]). It is difficult to escape the presently unfashionable conclusion, especially comparing with *trans*-$(PPh_3)_2Rh(CS)Cl$, that our short mutually *trans*-Rh–P bond lengths are caused by significant Rh–P (*d–d*) π-bonding in this compound.

TABLE 6

Mutually *trans*-rhodium–phosphorus bond lengths

Compound	Oxidation state	Geometry	Rh–P length (Å)	Ref.
$(PPh_3)_2Rh[NC(CF_3)_2][C(NMeCH_2)_2]$	I	Square planar	2·290(4), 2·291(4)	[a]
$[(diphos)_2Rh]^+ClO_4^-$	I	Square planar	2·289(6), 2·310(6), 2·310(6), 2·313(7)	45
$(PBu^tPr^n{}_2)_2RhHCl_2$	III	Square pyramidal	2·31	43
$(PPh_3)_3RhCl$	I	Tetrahedrally distorted Square planar	2·315(8), 2·327(8)	37
$(PPh_3)_2Rh(CS)Cl$	I	Square planar	2·335(2), 2·337(2)	36
$(PPh_3)_2RhHCl(SiCl_3)$	III	Trigonal bipyramidal	2·332(4), 2·344(4)	38
$(PPh_3)_3RhH(CO)$	I	Trigonal bipyramidal	2·34(1)	42
$(PPh_3)_2RhI_2Me$	III	Square pyramidal	2·350(4)	44
$[(diphos)_2Rh(O_2)]^+[PF_6]^-$	I	Trigonal bipyramidal	2·354(4), 2·362(4)	39
$(PPh_3)_2RhCl(CO)(SO_2)$	I	Tetragonal pyramidal	2·367(2), 2·371(2)	38
$(PEt_3)_2RhCl_3(CHNMe_2)$	III	Octahedral	2·368(3), 2·372(3)	40
$(PPh_3)_2RhCl(C_2H_4)$	I	Tetrahedrally distorted Square planar	2·370(8), 2·374(8)	37
$(PBu^n{}_3)_2P(OMe)_3RhCl_3$	III	Octahedral	2·379(5), 2·400(5)	41

[a] This work.

The geometry associated with the triphenylphosphine groups agrees well with that observed in free triphenylphosphine.[47]

Assuming an increase in atomic radius of Rh^I compared with Rh^{III} of 0·06 Å (*vide supra*) the presently established Rh^I–C_{carb} distance of 2·006(15) Å compares favourably with the Rh^{III}–C_{carb} distances of 1·961(11) Å in $[RhCl_3(PEt_3)_2(CHNMe_2)]$ [40] and 1·968(13) Å in $[RhI_3(CO)CPhNMeCPhNMe]$.[13]

The geometry of the carbene ligand is similar to that already determined for *cis*- and *trans*-$PtCl_2[C(NPhCH_2)_2]PEt_3$ [48] with the exception that in the *cis*-form of the latter the C_{carb}–N bonds are constrained crystallographically to be equal whereas in the present case they appear to be different [1·308(17) and 1·402(18) Å], though account must be taken of the fact that the bond lengths quoted here have not been corrected for librational motion which is obviously present (see final anisotropic thermal parameters and Figure 2). The average of the two [1·355(18) Å] agrees well with the corresponding distances in the Pt isomers of 1·327(11) (*cis*-form) and 1·348(18) Å (average, *trans*-form) and is similar to other C_{carb}–N distances (1·31—1·38 Å) already determined.[11,49] As in the Pt isomers, the plane of the 5-membered carbene ring is approximately perpendicular to the coordination plane of the metal.

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EXPERIMENTAL

The preparation of starting materials and general techniques have been described elsewhere.[13,14,21]

Reaction of [1,1-*Bis(trifluoromethyl)methyleneamido*]*tris(triphenylphosphine)rhodium*(I) *with Diphenyldiazomethane.*—The rhodium complex (0·200 g, 0·19 mmol) was added to a stirred solution of diphenyldiazomethane (0·037 g, *ca.* 0·19 mmol) in benzene (40 ml). The deep red-brown reaction mixture was stirred for 8 h at room temperature. The volume of solvent was reduced to *ca.* 10 ml and n-hexane (40 ml) was added to this solution to give a yellow precipitate, which was filtered off and shown (i.r.) to be largely unchanged rhodium methyleneamide. The filtrate, when cooled to −30°, yielded a second crop of the starting rhodium complex. The mother liquor was shown to contain mainly unchanged diphenyldiazomethane.

Similar quantities of starting materials were heated at 70° for 24 h. Addition of n-hexane (30 ml) to the concentrated benzene solution gave a dirty tan precipitate, which was filtered off and shown (i.r.) to be identical to the product obtained by heating the rhodium methyleneamide alone in benzene. The filtrate contained none of the starting diphenyldiazomethane.

Reaction of 1,1-*Bis(trifluoromethyl)methyleneamino(trimethyl)stannane with* trans-*Chloro*(1,3-*di*-p-*tolylimidazolidin*-2-*ylidene*)*bis(triphenylphosphine)rhodium*(I).—The tin reagent (0·20 ml, 1·0 mmol) was added (by pipette) to a stirred solution of the rhodium complex (0·456 g, 0·50 mmol) in benzene (50 ml). The reaction mixture was heated under reflux for 1 h, solvent was removed under reduced pressure, and the residue was washed with n-hexane (2 × 30 ml) to give, as an air-stable orange powder, trans-[1,1-*bis(trifluoromethyl)methyleneamido*]*bis(triphenylphosphine)*(1,3-*di*-p-*tolylimidazolidin*-2-*ylidene*)*rhodium*(I) (0·42 g, 80%).

Reaction between [1,1-*Bis(trifluoromethyl)methyleneamido*]-*tris(triphenylphosphine)rhodium*(I) *and* 1,1′,3,3′-*Tetramethyl*-2,2′-*bi-imidazolidinylidene*.—There was no reaction between the rhodium complex (0·527 g, 0·5 mmol) and the olefin (0·294 g, 1·5 mmol) in xylene (50 ml) during 16 h at 49°. There was, however, a rapid reaction when the mixture was heated at 120—130° for *ca.* 5 min. The product was recrystallised (xylene–hexane) and identified as trans-[1,1-*bis(trifluoromethyl)methyleneamido*]*bis(triphenylphosphine)*(1,3-*dimethylimidazolidin*-2-*ylidene*)*rhodium*(I) (>80%). In this way, suitable crystals were obtained for the *X*-ray structure determination.

Reaction of 1,1-*Diphenylmethyleneamidolithium with Chromium Hexacarbonyl.*—The lithium compound (10·0 mmol) in diethyl ether (100 ml) was added dropwise during 1 h to a slurry of chromium hexacarbonyl (2·2 g, 10·0 mmol) in diethyl ether (200 ml). When addition was completed, the reaction mixture was stirred for 1 h at room temperature. Solvent was then removed under reduced pressure and was replaced with methylene dichloride (50 ml). To this solution, triethyloxonium tetrafluoroborate (1·90 g, 10·0 mmol) in methylene dichloride (50 ml) was then added dropwise, and the red solution was stirred for a further 1 h. Solvent was removed under reduced pressure to give an oily orange-brown solid, which was extracted into n-hexane (3 × 100 ml). The combined extracts were reduced to *ca.* 50 ml and cooling to −30° afforded buff crystals, shown by analysis to be slightly impure chromium hexacarbonyl. The solution was filtered and more solvent was removed from the filtrate. The concentrated solution was recooled to −30° to give as bright red crystals [*diphenylimino(ethoxy)methylidene*]*pentacarbonylchromium*(0) (1·7 g, 40%) m.p. 88—90° [Found: C, 58·6; H, 3·6; N, 3·3%; *M* (mass spectrometrically), 429. $C_{21}H_{15}CrNO_6$ requires C, 58·7; H, 3·5; N, 3·3%; *M*, 429], ν(C:O) (hexane), 2062, 1940, 1930 cm^{-1}.

Lack of Reaction between 1,1-*Diphenylmethyleneamino(trimethyl)silane and Chromium Hexacarbonyl.*—The silane (0·205 g, *ca.* 0·2 ml, 0·8 mmol) in methylene dichloride (10 ml) was added dropwise during 5 min to a stirred solution of chromium hexacarbonyl (0·220 g, 1·0 mmol) in methylene dichloride (10 ml) at 0°. There was no colour change. The solution was allowed to warm to room temperature and was stirred for a further 5 h. Methylene dichloride was removed under reduced pressure and the residue was washed with n-hexane to give an almost quantitative yield of starting chromium hexacarbonyl.

Similarly, there was no significant reaction when a slurry of chromium hexacarbonyl in n-hexane was stirred at room temperature with 1,1-bis(trifluoromethyl)methyleneamino-(trimethyl)stannane.

Reaction of N-*Methylbenzimidoyl Chloride with Tetrakis(triphenylphosphine)platinum*(0).—The chloride (0·15 ml, *ca.* 1·1 mmol) was added, by pipette, to a stirred solution of the Pt complex (1·243 g, 1·0 mmol) in benzene (30 ml) at 25°. The reaction mixture was stirred (1 h) at room temperature and was then heated under reflux for 3 h. Solvent was removed under reduced pressure to give an oily yellow solid, which was redissolved in benzene (*ca.* 8 ml) and reprecipitated with n-hexane (30 ml). The solid was filtered off from the pale yellow solution and reprecipitated from benzene solution using n-hexane. The precipitate was again filtered off and added to benzene (40 ml). In this way, a white precipitate and a pale yellow solution were obtained. The solution was filtered and benzene was removed from the filtrate. Benzene (30 ml) was added to the filtrate residue to give again a small quantity of white solid and a pale yellow solution. The solution was filtered and solvent was once more removed from the filtrate and the cycle of operations was repeated. Eventually a pale yellow benzene solution was obtained. To this, n-hexane (30 ml) was added to give a pale yellow powder, which was filtered off, washed with n-hexane (2 × 30 ml), and dried (1 h, 0·001 mmHg). The product, an off-white powder, was chloro(*N*-methylbenzimidoyl)bis(triphenylphosphine)platinum(II) (*ca.* 15% yield), m.p. 230—232° (Found: C, 60·3; H, 4·5; N, 1·7. Calc. for $C_{44}H_{38}ClNP_2Pt$: C, 60·5; H, 4·4; N, 1·6%), ν_{CN} 1595 cm^{-1}, ν(PtCl) 265 cm^{-1}.

Reaction of $Pt(Cl)(PhC{:}NMe)(PPh_3)_2$ *with Hydrogen Chloride.*—Hydrogen chloride (0·12 mmol) in diethyl ether (0·05 ml) was added to a solution of the platinum complex (0·100 g, 0·11 mmol) in benzene (25 ml) at *ca.* 5°. The solution was stirred for 2 h at room temperature, the solvent was removed under reduced pressure, and the residue was washed with n-hexane to give, as a white powder, the 1 : 1 *complex* (100% yield), m.p. 251—254° (Found: C, 60·6; H, 4·7; N, 1·6. $C_{44}H_{39}Cl_2NP_2Pt$ requires C, 60·5; H, 4·5; N, 1·6%), ν(PtCl) 313 cm^{-1}.

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