Complexes of the Platinum Metals. Part IV.[1] 1,3-Diaryltriazenido Derivatives

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1,3-Diaryltriazenes, ArN:N·NHAr, react with hydrido or low-oxidation state phosphine complexes of the platinum metals to afford products containing monodentate or chelate 1,3-diaryltriazenido ($ArNNNAr^-$) ligands. Highly coloured, air stable, crystalline products synthesised in this manner include 1,3-diaryltriazenido derivatives of ruthenium: $Ru(ArNNNAr)_2(PPh_3)_2$, $RuH(ArNNNAr)(CO)(PPh_3)_2$, $RuCl(ArNNNAr)(CO)(PPh_3)_2$; osmium: $Os(ArNNNAr)_2(PPh_3)_2$, $OsH(ArNNNAr)(CO)(PPh_3)_2$, $OsH_3(ArNNNAr)(PPh_3)_2$; rhodium: $RhH_2(ArNNNAr)(PPh_3)_2$, $Rh(ArNNNAr)_3$, $RhCl(ArNNNAr)_2(PPh_3)$, $Rh(NO)(ArNNNAr)_2(PPh_3)$, $Rh(ArNNNAr)(CO)(PPh_3)_2$ $[Rh(Ph_2PCH_2CH_2PPh_2)_2][ArNNNAr]$; iridium: $IrH_2(ArNNNAr)(PPh_3)_2$, $IrHCl(ArNNNAr)(PPh_3)_2$; palladium; *cis*- and *trans*-$Pd(ArNNNAr)_2(PPh_3)_2$; and platinum: *cis*- and *trans*-$Pt(ArNNNAr)_2(PPh_3)_2$, $Pt(ArNNNAr)_2[Ph_2P(CH_2)_nPPh_2]$ (n = 2—4), and $PtCl(ArNNNAr)(PR_3)_2$ (R = Et or Ph). The new complexes are characterised, and their stereochemistry determined, by i.r. and n.m.r. spectroscopy.

ALTHOUGH the ligand properties of carboxylate and allyl anions have been extensively studied those of the isoelectronic 1,3-diaryltriazenide anions have received remarkably little attention. 1,3-Diaryltriazenido derivatives, synthesised by reacting silver triazenides[2] with the appropriate metal halides, have been reported for titanium, zirconium, iron, and a variety of main-group elements. Reactions of 1,3-diaryltriazenes with metal acetates, or with metal halides in the presence of sodium acetate or hydroxide have been employed to obtain triazenido derivatives of nickel, palladium, platinum, and copper.[3-5] Structures involving monodentate,[5] chelate,[3,4] and bridging[5] triazenido ligands have been proposed for the derivatives mentioned above and recent *X*-ray diffraction studies on mononuclear $Co(PhNNNPh)_3$,[6] and binuclear $[Cu(PhNNNPh)]_2$[7] and $[Ni(PhNNNPh)_2]_2$[8] have confirmed the presence of chelate and bridging triazenido ligands respectively.

In this paper we describe a novel and very convenient general synthesis for an extensive range of platinum metal triazenido derivatives containing phosphine, carbonyl, nitrosyl, and hydride ligands. The new complexes, all of which are monomeric, are assigned structures containing monodentate or chelate triazenido ligands on the basis of i.r. and n.m.r. spectroscopic evidence. Prior to the preliminary publication of this work[9,10] no triazenido derivatives of rhodium, iridium, ruthenium, and osmium had been reported. However while this study was in progress Knoth[11] described the synthesis of rhodium, iridium, and ruthenium triazenido derivatives, including some of the products discussed here, by the reaction of lithium triazenido salts with metal halide complexes.

Preparative Methods.—The first and most important group of syntheses employed in this work involve the reactions of 1,3-diaryltriazenes with preformed hydrido or low-oxidation state phosphine complexes of the platinum metals in benzene or alcoholic solvents. In each instance the stoicheiometry of the reaction corresponds to the oxidative addition of the triazene N–H bond across the platinum metal centre, (1). This process is often accompanied by elimination of molecular hydrogen, (2), or a neutral ligand, (3); and, when performed in alcoholic media, by the replacement of chloride ligands by hydride, (4). This last process, which proceeds in the

$$ML_x + ArN{:}N{\cdot}NHAr \longrightarrow MH(ArNNNAr)L_x \qquad (1)$$

$$MHL_x + ArN{:}N{\cdot}NHAr \longrightarrow M(ArNNNAr)L_x + H_2 \qquad (2)$$

$$MHL_x + ArN{:}N{\cdot}NHAr \longrightarrow MH_2(ArNNNAr)L_{x-1} + L \qquad (3)$$

$$MCL_x \longrightarrow MHL_x \qquad (4)$$

(M = platinum metal; L = CO, PPh_3, *etc.*)

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[8] M. Corbett and B. F. Hoskins, *Chem. Comm.*, 1968, 1602.

[9] S. D. Robinson and M. F. Uttley, *Chem. Comm.*, 1971, 1315.

[10] S. D. Robinson and M. F. Uttley, *J.C.S. Chem. Comm.*, 1972, 184.

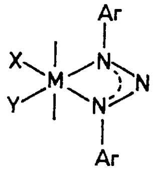
[11] W. H. Knoth, *Inorg. Chem.*, 1973, **12**, 38.

presence of an excess of triazene and requires the use of an alcoholic solvent, probably involves a base–alcohol ' reduction ' step, similar to those which occur in metal hydride synthesis, in which the excess of triazene functions as the base.

The second group of syntheses involves reaction of 1,3-diaryltriazenes with metal phosphine complexes generated *in situ*. In these reactions 1,3-diaryltriazenido complexes are conveniently, albeit somewhat inefficiently, synthesised by a single step process involving direct reduction of the appropriate metal halide with alcoholic base in the presence of an excess of triphenylphosphine and 1,3-diaryltriazene. With sodium chloro-osmate this single step synthesis gave a series of osmium(II) complexes $Os(ArNNNAr)_2(PPh_3)_2$ not otherwise readily accessible. However, with rhodium, iridium, and ruthenium chlorides the products isolated from the single step syntheses are identical with those obtained from $RhH(PPh_3)_4$, $IrH_3(PPh_3)_3$, and $RuH_2(PPh_3)_4$ respectively; and it appears probable that the formation of these latter species by base–alcohol reduction of the metal halides in the presence of an excess of triphenylphosphine [12] is an intermediate step in these reactions. Details of individual syntheses are given in the Experimental section.

One aspect of these syntheses, the cleavage of N–H bonds, merits further comment. Oxidative addition reactions are known to occur with a wide variety of substrates; [13] however examples involving cleavage of N–H bonds are relatively rare.[14] The facile cleavage of N–H bonds in 1,3-diaryltriazenes probably owes much to the resonance stabilisation of the triazenido anions $(ArN\overset{\cdots}{=}N\overset{\cdots}{=}NAr)^-$.

Spectroscopic Data.—Before discussing the structure and properties of individual complexes we review the general approach used to arrive at the structural assignments, and comment upon our previous, somewhat controversial, i.r. evidence. Molecular weight studies indicate that, in solution at least, all the 1,3-diaryltriazenido complexes reported in this work are monomeric and, with the exception of the ionic species $[Rh(P\text{–}P)_2]$-$[ArNNNAr]$, may therefore be presumed to contain monodentate or bidentate (chelate) triazenido ligands. Structures involving monodentate,[5] chelate,[3,4] and bridging [5] 1,3-diaryltriazenido ligands have previously been postulated, however prior to the present study no attempt to distinguish between these three modes of bonding on the basis of i.r. spectroscopy had been reported. We previously noted [9] that the mononuclear, covalent 1,3-diaryltriazenido complexes discussed in this paper divided into two distinct classes on the basis of their i.r. spectra. Class A complexes (using the nomenclature adopted by Knoth [11]), which included the derivatives of ruthenium(II), osmium(II) and (IV), iridium(III), and rhodium(III), gave spectra containing bands at 1260—1300 and 1580—1600 cm^{-1} attributable to the 1,3-diaryltriazenido ligands, and were formulated as chelate triazenido derivatives. Class B compounds, which included derivatives of palladium(II), platinum(II), and rhodium(I) showed bands at *ca.* 1150, 1190—1210, 1260—1300, and 1580—1600 cm^{-1} which were attributed to the presence of monodentate 1,3-diaryltriazenido ligands. Bridging 1,3-diaryltriazenido ligands also gave i.r. spectra typical of class B compounds; [11] however the presence of bridging ligands had previously been eliminated by the molecular weight studies, and this mode of co-ordination was therefore not considered further. These empirical i.r. criteria, permitted rational and self-consistent assignments of structure to be made for the sixty compounds reported in this work and were employed for this purpose in our preliminary communications.[9,10] The assignments made on this basis are in accord with the preferred co-ordination numbers for the species concerned, namely seven for osmium(IV) multihydrides, six for ruthenium(II), osmium(II), rhodium(III), and iridium(III), and four for palladium(II) and platinum(II). The rhodium(I) species $Rh(ArNNNAr)$-$(CO)(PPh_3)_2$ can be accommodated equally well as monodentate (four-co-ordinate) or bidentate (five-co-ordinate) triazenido derivatives. However, in his recent paper on 1,3-diaryltriazenido derivatives of rhodium, iridium, and ruthenium, Knoth [11] has described new triazenido complexes which apparently do not conform to the i.r. criteria discussed above. In particular, five series of complexes of general formulae $Rh(ArNNNAr)(C_8H_{12})$, $Rh(ArNNNAr)(PPh_3)_2$, $Rh(ArNNNAr)(CO)(PPh_3)_2$, $Ir(ArNNNAr)(CO)(PPh_3)_2$, and $RuH(ArNNNAr)$-$(PPh_3)_3$, which showed i.r. spectra of the form hitherto associated with monodentate triazenido ligands, were formulated by Knoth as chelate triazenido derivatives on the basis of chemical and n.m.r. evidence. In several instances this evidence is inconclusive; however for two series of complexes $Rh(ArNNNAr)(PPh_3)_2$ and $Rh(ArNNNAr)(C_8H_{12})$ it is overwhelming. If correctly formulated, these latter species, which are monomeric, must either contain chelate triazenido ligands or adopt a most improbable three-co-ordinate geometry. In the light of these observations our original i.r. criteria for distinguishing between mono- and bidentate triazenido ligands, and hence the assignments based upon them, must be considered suspect. However, with one possible exception [complexes of stoicheiometry $Rh(ArNNNAr)$-$(CO)(PPh_3)_2$] these assignments can be substantiated using more conventional i.r. and n.m.r. spectral data, and making reasonable assumptions concerning the co-ordination numbers of the metal ions concerned. Stereochemical assignments were also greatly facilitated by the



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[12] N. Ahmad, S. D. Robinson, and M. F. Uttley, *J.C.S. Dalton*, 1972, 843.

[13] J. P. Collman and W. R. Roper, *Adv. Organometallic Chem.*, 1968, **7**, 53.

[14] D. M. Roundhill, *Inorg. Chem.*, 1970, **9**, 254.

n.m.r. spectra of the triazenido ligands; symmetrically co-ordinated 1,3-di-*p*-tolyl- and 1,3-di(*p*-methoxyphenyl)-triazenido ligands ($X = Y$) each show a single methyl resonance whereas those in an asymmetric environment ($X \neq Y$) give rise to two independent methyl resonances. Structural assignments given below for individual compounds are based on these criteria.

Structure and Properties of 1,3-*Diaryltriazenido Complexes.*—The new 1,3-diaryltriazenido derivatives of the platinum metals are all highly coloured, air-stable, crystalline solids. Unlike the recently reported [2] 1,3-diphenyltriazenido derivatives of titanium, zirconium, and iron, they show no appreciable tendency to undergo hydrolysis. However the bis(1,3-diaryltriazenido) derivatives are slowly attacked by chlorinated hydrocarbons. There is no evidence to suggest that any of the compounds discussed are liable to explosive decomposition when subjected to heat or percussion.

Ruthenium Triazenido Complexes.—$Ru(ArNNNAr)_2(PPh_3)_2$. These bright red microcrystalline complexes are sparingly soluble in organic solvents, and are slowly attacked by chlorinated hydrocarbons. Recrystallisation from the latter solvents is accompanied by some decomposition and yields of purified product are correspondingly low. The proton n.m.r. spectra of the 1,3-di-*p*-tolyl- and 1,3-di(*p*-methoxyphenyl)-triazenido derivatives are temperature independent and each show a single resonance attributable to four equivalent methyl groups. Assuming that the ruthenium(II) ion achieves the usual octahedral co-ordination, the n.m.r. spectra are indicative of the symmetrical chelate structure (I; M = Ru).

$RuH(ArNNNAr)(CO)(PPh_3)_2$. These orange-yellow crystalline complexes were recrystallised from dichloromethane–ethanol or benzene–ethanol, and were frequently obtained as benzene solvates from the latter solvents. The expected band attributable to ν(RuH) could not be detected in the i.r. spectra of these complexes, and is probably masked by the ν(CO) vibration which occurs at *ca.* 1920 cm^{-1} in each case. However the presence of a hydride ligand *cis* to two equivalent phosphorus nuclei is unambiguously established for each complex by the presence of a high field n.m.r. triplet [*ca.* τ 22·0; $^2J(PH)$ *ca.* 20 Hz]. The low-field n.m.r. spectra of the di-*p*-tolyl- and di(*p*-methoxyphenyl)-triazenido derivatives each show the presence of two non-equivalent methyl groups indicative of a chelate triazenido ligand in an asymmetric environment. On the basis of this evidence these complexes can be assigned stereochemistry (II; M = Ru).

$RuCl(ArNNNAr)(CO)(PPh_3)_2$. These products are less soluble than their hydrido analogues, and deposit from benzene solution as solvates. Their i.r. spectra each show a strong band at *ca.* 1920 cm^{-1} attributable to ν(CO), and the n.m.r. spectrum of the di-*p*-tolyltriazenido derivative indicates the presence of asymmetric triazenido ligands. On the basis of this evidence these complexes are assigned stereochemistry (III; M = Ru).

Osmium Triazenido Complexes.—$Os(ArNNNAr)_2(PPh_3)_2$ *and* $OsH(ArNNNAr)(CO)(PPh_3)_2$. These air-stable crystalline osmium(II) complexes are assigned stereochemistries (I) and (II) respectively (M = Os) on the basis of i.r. and n.m.r. data similar to those discussed for their ruthenium analogues.

$OsH_3(ArNNNAr)(PPh_3)_2$. These products were obtained by reacting $OsH_4(PPh_3)_3$ with 1,3-diaryltriazenes in boiling 2-methoxyethanol; and are formulated as osmium(IV) trihydride species rather than osmium(II) monohydrides $OsH(ArNNNAr)(PPh_3)_2$ on the basis of spectral evidence. Thus their i.r. spectra each show a group of ν(OsH) vibrations similar to those observed for other osmium(IV) multihydrides; [15-17] and their high-field n.m.r. spectra each comprise a triplet of relative intensity three, with chemical shift (*ca.* τ 19) and coupling constant [$^2J(PH)$ = *ca.* 13 Hz] typical of osmium(IV) multihydride species. The apparent magnetic equivalence of the hydride ligands in these osmium(IV) trihydrides cannot be accounted for in terms of a rigid seven-co-ordinate structure, and is therefore taken as evidence of stereochemical non-rigidity similar to that recently reported for several other seven-co-ordinate osmium multihydride species.[15-17]

These osmium(IV) trihydrides show remarkable stability towards dihydrogen elimination. The 1,3-diphenyltriazenido derivative was recovered unchanged after treating with an excess of triphenylphosphine in boiling toluene; in contrast the hydrides $OsH_4(PR_3)_3$ readily lose a molecule of dihydrogen under similar conditions.[17] The unusual stability of these and other high oxidation state triazenido-hydrido derivatives (see below) may well arise from the delocalisation of π-electron density from the triazenido ligands into empty metal t_{2g} orbitals.

Rhodium Triazenido Complexes.—$RhH_2(ArNNNAr)(PPh_3)_2$. These orange or yellow complexes were prepared by reacting $RhH(PPh_3)_4$ with 1,3-diaryltriazenes, or by a single step synthesis involving base–alcohol reduction of $RhCl_3,3H_2O$ in the presence of an excess of triphenylphosphine and a triazene. An alternative synthesis, recently described,[11] involves hydrogenation of the rhodium(I) species $Rh(ArNNNAr)(PPh_3)_2$. The high-field n.m.r. spectra of the rhodium(III) triazenido derivatives each comprise a triplet of doublets [$^2J(PH)$ = *ca.* 16·0 Hz; $^1J(RhH)$ = *ca.* 17 Hz] centred at *ca.* τ 27·3 and indicative of equivalent hydride ligands *cis* to a pair of equivalent phosphorus nuclei. The presence of a pair of mutually *cis* hydride ligands is confirmed by the presence of two i.r. bands attributable to ν(RhH) in the range of 2020—2080 cm^{-1}. Finally the low-field n.m.r. spectra of the 1,3-di-*p*-tolyl- and 1,3-di(*p*-methoxyphenyl)-triazenido derivatives reveal the presence of symmetrical triazenido ligands (equivalent methyl groups) and hence establish stereochemistry (IV; M = Rh) for these complexes. Rhodium(III) dihydrido

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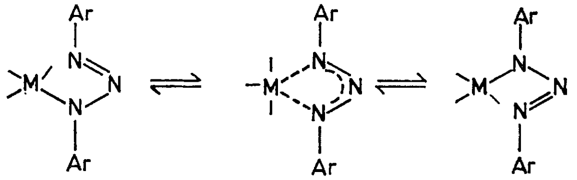
[15] J. J. Levison and S. D. Robinson, *J. Chem. Soc.* (*A*), 1970, 2947.

[16] P. G. Douglas and B. L. Shaw, *J. Chem. Soc.* (*A*), 1970, 334.

[17] B. Bell, J. Chatt, and G. J. Leigh, *J.C.S. Dalton*, 1973, 997.

complexes have been widely postulated as intermediates in catalytic hydrogenation reactions, and a number of isolable examples have been reported.[18] However the remarkable stability with respect to dihydrogen loss displayed by the present examples is unexpected, and probably indicates that the triazenido ligand is again stabilising a relatively high oxidation state hydride complex by acting as a strong σ- and/or π-electron donor [see osmium(IV) above].

$Rh(ArNNNAr)(CO)(PPh_3)_2$. These complexes were prepared by reacting $RhH(CO)(PPh_3)_3$ with 1,3-diaryltriazenes, and were obtained as red or yellow crystals from benzene–methanol. Compounds of this general formula have also recently been synthesised by carbonylation of the rhodium(I) complexes $Rh(ArNNNAr)(PPh_3)_2$.[11] In our preliminary report [9] these products were formulated, on the basis of i.r. evidence, as four-co-ordinate rhodium(I) complexes containing monodentate 1,3-diaryltriazenido ligands. The observed magnetic equivalent of the methyl groups in the 1,3-di-*p*-tolyl-triazenido derivative, which was maintained at the lowest accessible temperature (−60°), was attributed [10] to a rapid intramolecular triazenido ligand exchange process involving a readily accessible five-co-ordinate chelate intermediate:



However, as noted above, Knoth [11] has recently challanged the i.r. criteria upon which this assignment rests, and has proposed an alternative five-co-ordinate chelate triazenido structure for the complexes $Rh(ArNNNAr)(CO)(PPh_3)_2$. Knoth seeks to discount our fluxional monodentate structure on the grounds that the proton decoupled ^{19}F n.m.r. spectra of mixtures containing $Rh(ArNNNAr)(CO)(PPh_3)_2$ and $Ir(ArNNNAr)(CO)(PPh_3)_2$ or $Li(ArNNNAr)$ ($Ar = p\text{-}C_6H_4F$) show no evidence of exchange broadening. We have noted [10] the absence of exchange broadening in the n.m.r. spectra of similar complex mixtures, however these observations do not exclude the possible occurrence of an intramolecular, as opposed to an intermolecular, exchange process of the type proposed above. We therefore conclude that on the available evidence it is not possible to differentiate between the alternative four- and five-co-ordinate structures for the complexes $Rh(ArNNNAr)(CO)(PPh_3)_2$. In this context it is interesting to note that a recent controversy [19,20] concerning the stereochemistry of the closely related complex $Rh(OCOCH_3)(CO)(PPh_3)_2$ has been resolved in favour of a square-planar structure involving monodentate acetate ligands.[21,22]

$[Rh(Ph_2PCH_2CH_2PPh_2)_2][ArNNNAr]$. The diphosphine $Ph_2PCH_2CH_2PPh_2$ was reacted with the rhodium(I) triazenido complexes $Rh(ArNNNAr)(CO)(PPh_3)_2$ in an attempt to obtain the five-co-ordinate species $Rh(ArNNNAr)(Ph_2PCH_2CH_2PPh_2)_2$ containing non-fluxional monodentate triazenido ligands. However n.m.r. spectra of the products isolated revealed the presence of symmetrical triazenido moieties, and the solubility behaviour suggested that the complexes were probably salts of the form $[Rh(Ph_2PCH_2CH_2PPh_2)_2][ArNNNAr]$. This formulation was confirmed by conducitivity measurements performed using 10^{-3}M methyl cyanide solutions ($\Lambda = 127\ \Omega^{-1}\ cm^2\ mol^{-1}$) and by anion exchange reactions. The corresponding reactions of the carboxylates $Rh(OCOR)(CO)(PPh_3)_2$ with $Ph_2PCH_2CH_2PPh_2$ have recently been reported to yield similar ionic products.[22]

$RhCl(ArNNNAr)_2(PPh_3)$. These red-brown crystalline rhodium(III) derivatives were obtained under surprisingly mild conditions simply by reacting $RhCl(PPh_3)_3$ with triazenes in cold benzene. The n.m.r. spectrum of the 1,3-di-*p*-tolyltriazenido derivative, which showed the presence of two equivalent (τ 8·10) and two non-equivalent (τ 8·02, 7·92) methyl groups, is indicative of stereochemistry (V) for these complexes.

$Rh(ArNNNAr)_2(NO)(PPh_3)$. The reaction of $Rh(NO)(PPh_3)_3$ with 1,3-di-*p*-tolyltriazene affords the nitrosyl derivative $Rh(ArNNNAr)_2(NO)(PPh_3)$ (Ar = *p*-tolyl). However attempts to obtain related products containing other triazenido ligands were unsuccessful. The i.r. spectrum of the new nitrosyl complex has a band at 1603 cm^{-1} attributable to ν(NO), and in good agreement with similar assignments made for the related rhodium nitrosyl halide $RhX_2(NO)(PPh_3)_2$ [23] and carboxylate $Rh(OCOR)_2(NO)(PPh_3)_2$ [22] derivatives. The n.m.r. spectrum of the new complex contains a single methyl resonance and is consistent with, but does not prove the presence of, a symmetrical structure (VI).

$Rh(ArNNNAr)_3$ [Ar = *p*-tolyl]. This complex is the first example of a tris(triazenido) derivative of a platinum metal; similar complexes have been previously reported for iron(III) and cobalt(III). A mono-nuclear, tris(chelate) structure has been established for the cobalt derivative by *X*-ray diffraction.[6]

Iridium Triazenido Complexes.—$IrH_2(ArNNNAr)(PPh_3)_2$. These red or yellow crystalline complexes are assigned stereochemistry (IV; M = Ir) on the basis of i.r. and n.m.r. data (Table 2) similar to those recorded for the analogous rhodium dihydrides.

$IrHCl(ArNNNAr)(PPh_3)_2$. These products are obtained as air-stable, crystalline, yellow or orange solids, and are unequivocally assigned stereochemistry (VII) on the basis of their n.m.r. spectra which indicate the presence of asymmetric triazenido ligands, together with a hydride *cis* to two equivalent phosphorus nuclei.

[18] H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, 1972, **72**, 231.

[19] R. W. Mitchell, J. D. Ruddick, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1971, 3224.

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[22] S. D. Robinson and M. F. Uttley, *J.C.S. Dalton*, **1973**, **1912**.

[23] S. D. Robinson and M. F. Uttley, *J. Chem. Soc.* (*A*), 1971, 1254.

TABLE 1

Analytical, molecular weight, and m.p. data for 1,3-diaryltriazenido complexes of the platinum metals

				Analytical data (%) [d]		
Complex [a]	Tri [b]	M.p. (t/°C) [c]	M [d]	C	H	N
$\mathrm{Ru(tri)_2(PPh_3)_2}$	dpt	178—180	1032 (1017)	70·7 (70·8)	5·1 (4·9)	8·2 (8·2)
	dtt	198—199	885 (1073)	71·8 (71·5)	5·6 (5·4)	7·9 (7·8)
	dmt	167—169	980 (1137)	68·1 (67·5)	5·1 (5·1)	7·3 (7·4)
	dct	200—202	1140 (1155)	62·2 (62·3)	3·8 (4·0)	
$\mathrm{RuH(tri)(CO)(PPh_3)_2}$	dpt	212—116	809 (850)	68·7 (69·2)	4·7 (4·7)	4·7 (4·9)
	dtt	217—218	865 (878)	70·0 (69·8)	5·4 (5·1)	4·9 (4·8)
	dmt	203—206	887 (910)	67·5 (67·6)	5·3 (4·9)	5·0 (4·6)
	dct	266—268	902 (919)	64·4 (63·9)	4·4 (4·2)	4·1 (4·5)
	tmt	222—226		68·2 (68·5)	5·0 (4·9)	4·7 (4·7)
$\mathrm{RuCl(tri)(CO)(PPh_3)_2}$	dtt	260—262	885 (912)	69·5 (69·0)	5·3 (5·1)	4·1 (4·2)
	dmt	260—263		67·1 (66·9)	5·5 (4·8)	4·2 (4·1)
	tmt	229—234		68·4 (68·0)	5·5 (4·9)	4·3 (4·1)
$\mathrm{Os(tri)_2(PPh_3)_2}$	dpt	>300		64·7 (65·1)	5·0 (4·5)	7·5 (7·6)
	dtt	>300	1105 (1162)	66·1 (66·1)	5·0 (5·0)	6·7 (7·2)
	dct	>300		57·4 (57·9)	4·0 (3·7)	
$\mathrm{OsH(tri)(CO)(PPh_3)_2}$	dtt	235—238	924 (967)	63·5 (63·3)	5·1 (4·7)	4·1 (4·3)
	dmt	225—227	1059 (999)	60·9 (61·3)	4·8 (4·5)	4·0 (4·2)
	dct	300	991 (1008)	58·2 (58·3)	4·3 (3·9)	4·1 (4·1)
$\mathrm{OsH_3(tri)(PPh_3)_2}$	dpt	198—201	920 (912)	65·5 (65·4)	5·1 (4·9)	4·1 (4·2)
	dtt	187—188	940 (1008)	64·7 (63·7)	5·0 (5·0)	
	dmt	192—193	1019 (972)	62·0 (61·7)	5·6 (4·7)	4·5 (4·3)
	dct	193—195	1016 (981)	58·8 (58·7)	5·4 (4·1)	4·5 (4·3)
	tmt	170—180		62·9 (62·7)	5·2 (4·9)	4·4 (4·4)
$\mathrm{Rh(tri)_3}$	dtt			64·5 (65·0)	5·4 (5·45)	16·35 (16·25)
$\mathrm{RhH_2(tri)(PPh_3)_2}$	dpt	144—147	745 (825)	69·7 (69·9)	4·8 (5·0)	5·0 (5·1)
	dtt	106—111		69·9 (70·3)	5·5 (5·4)	4·7 (4·9)
	dct	142—145	904 (894)	64·0 (64·5)	4·3 (4·4)	4·8 (4·7)
	tmt	107—114		68·4 (69·0)	5·2 (5·3)	4·6 (4·8)
$\mathrm{Rh(tri)(CO)(PPh_3)_2}$	dpt	164—167	847 (851)	68·6 (69·1)	4·8 (4·7)	4·5 (4·9)
	dtt	161—163	808 (879)	69·4 (69·6)	4·9 (5·0)	4·8 (4·8)
	dct	175—176	892 (920)	64·6 (65·0)	4·3 (4·6)	4·6 (4·6)
	tmt	153—155		68·3 (68·3)	5·2 (5·0)	4·7 (4·7)
$\mathrm{RhCl(tri)_2(PPh_3)}$ [f]	dpt	200—201		64·1 (64·9)	4·3 (4·6)	10·5 (10·1)
	dtt	219—220	1010 (848)	65·8 (66·2)	5·0 (4·8)	9·8 (9·4)
	dct	240—242	958 (930)	55·2 (55·7)	3·5 (3·2)	9·1 (8·7)
$\mathrm{Rh(tri)(dppe)_2}$	dtt	264—270		70·3 (70·5)	5·6 (5·5)	3·3 (3·7)
$\mathrm{Rh(tri)_2(NO)(PPh_3)}$	dtt	144—151		65·3 (65·5)	5·1 (5·1)	11·3 (11·6)
$\mathrm{IrH_2(tri)(PPh_3)_2}$	dpt	212—220		63·3 (63·0)	4·7 (4·6)	4·4 (4·6)
	dtt	170—195	975 (942)	64·6 (63·7)	4·9 (4·9)	4·3 (4·4)
	dct	253—256		58·8 (58·6)	4·0 (4·1)	4·2 (4·2)
	tmt	209—210		62·8 (62·6)	4·9 (4·8)	3·9 (4·4)
$\mathrm{IrHCl(tri)(PPh_3)_2}$	dpt	220—222	975 (948)	61·1 (60·7)	4·8 (4·3)	4·1 (4·4)
	dtt	263—265	979 (976)	61·1 (61·5)	4·6 (4·6)	4·0 (4·3)
	dct	283—285	1020 (1017)	56·6 (56·7)	3·9 (3·8)	4·1 (4·1)
$\mathrm{Pt(tri)_2(PPh_3)_2}$	dpt	173—198	1094 (1111)	67·1 (66·6)	4·8 (4·7)	7·1 (7·0)
	dtt	206—207		65·7 (65·8)	5·0 (5·0)	7·4 (7·2)
	dmt	180—184		62·5 (62·4)	4·7 (4·7)	6·5 (6·8)
	dct	230—233	1213 (1249)	58·5 (57·6)	3·7 (3·7)	6·5 (6·7)
	tmt	193—194		64·7 (64·9)	5·2 (4·9)	7·1 (7·1)
$\mathrm{Pt(tri)_2(dppe)}$	dtt	255—258		62·0 (62·2)	5·2 (5·0)	7·8 (8·0)
$\mathrm{Pt(tri)_2(dppp)}$	dtt	245—249		63·0 (62·5)	5·2 (5·1)	7·8 (7·9)
$\mathrm{Pt(tri)_2(dppb)}$	dtt	235—244		64·8 (64·8)	5·6 (5·4)	7·0 (7·3)
$\mathrm{PtCl(tri)(PPh_3)_2}$	dtt	235—236	991 (978)	61·9 (61·3)	4·7 (4·5)	3·9 (3·6)
	dmt			59·2 (59·4)	4·4 (4·4)	3·8 (4·1)
	tmt	223—225		60·1 (60·3)	4·5 (4·4)	3·9 (4·2)
$\mathrm{PtCl(tri)(PEt_3)_2}$	dtt			45·6 (45·2)	6·5 (6·3)	5·8 (6·1)
$\mathrm{Pd(tri)_2(PPh_3)_2}$	dtt	186—187		70·7 (71·2)	5·2 (5·4)	7·9 (7·8)
	dmt	161—162		68·9 (68·8)	5·3 (5·5)	7·0 (6·9)
	dct	190—191	1159 (1160)	62·8 (62·1)	4·3 (3·9)	
	tmt	169—171		69·6 (69·1)	5·6 (5·2)	7·6 (7·5)
$\mathrm{Pd(tri)_2(dppp)}$	dtt	211—212		69·9 (70·0)	5·8 (5·7)	

[a] dppe = $\mathrm{Ph_2PCH_2CH_2PPh_2}$, dppp = $\mathrm{Ph_2PCH_2CH_2CH_2PPh_2}$, dppb = $\mathrm{Ph_2PCH_2CH_2CH_2CH_2PPh_2}$. [b] 1,3-Diaryltriazenido ligands: dpt = 1,3-diphenyl-, dtt = 1,3-di-*p*-tolyl-, dmt = 1,3-di-*p*-methoxyphenyl-, dct = 1,3-di-*p*-chlorophenyl-, tmt = 1-*p*-tolyl-3-*p*-methoxyphenyl-. [c] All m.p.s taken in air, and usually accompanied by decomposition. [d] Calculated figures in parentheses. [e] Solvated with 1 molecule of benzene. [f] Solvated with ½ molecule of benzene.

TABLE 2

I.r. and ^{1}H n.m.r. spectroscopic data for triazenido complexes of the platinum metals

Complex [a]	tri [a]	ν(MH)	ν(CO)	$\nu(\mathrm{tri})_1$ [b]	$\nu(\mathrm{tri})_2$ [b]	τ (MH) [c]	J(PH)	τ (CH_3)
$Ru(tri)_2(PPh_3)_2$	dpt			1267				
	dtt			1269				
	dmt			1281				6·63
	dct			1265				
$RuH(tri)(CO)(PPh_3)_2$	dpt		1918	1275		22·33	20·25	
	dtt		1927	1280, 1295		22·37	20·5	7·95, 7·83
	dmt		1908	1301, 1285		22·27	20·0	6·70, 6·62
	dct		1927	1285, 1269		22·64	20·0	
	tmt		1920	1293, 1278		22·31	20·5	7·94, 7·83, 6·71, 6·62
$RuCl(tri)(CO)(PPh_3)_2$	dtt		1928	1279				7·95, 7·89
	dmt		1928	1296				
	tmt		1923	1298, 1277				
$Os(tri)_2(PPh_3)_2$	dpt			1265				
	dtt			1267				7·82
	dct			1261				
$OsH(tri)(CO)(PPh_3)_2$	dtt	2004	1903	1282, 1292		22·85	18·5	7·87, 7·82
	dmt	2002	1901	1295		22·85	18·5	6·69, 6·62
	dct	2022	1904	1289, 1271		23·09	17·5	
$OsH_3(tri)(PPh_3)_2$	dpt	2102 1914		1275		19·35	13·5	
	dtt	2092 2072 1900		1275, 1288		19·32	13·0	7·92
	dmt	2098 2070 1900		1291, 1305		19·32	13·5	
	dct	2074 1906		1287, 1268		19·47	14·0	
	tmt	2092 2074 1894		1286		19·36	13·0	7·92 6·71
$RhH_2(tri)(PPh_3)_2$	dpt	2080 2048		1270		27·38	15·5	
	dtt	2038 2024		1295, 1279		27·35	15·5	
$RhH_2(tri)_2(PPh_3)_2$	dct	2044 2032		1289, 1268		27·36	16·0	
	tmt	2060 2022		1293, 1280		27·27	16·0	7·86 6·67
$Rh(tri)(CO)(PPh_3)_2$	dpt		1952	1293, 1278	1206			
	dtt		1940	1304, 1277	1213			7·83
	dct		1941	1294, 1271	1210			
	tmt		1945	1303, 1276	1209			7·85 6·64
$RhCl(tri)_2(PPh_3)$	dpt			1283				
	dtt			1301, 1289				8·10, 8·02, 7·92
	dct			1302, 1279				
$Rh(tri)(dppe)_2$	dtt			1190, 1180				
$Rh(tri)_2(NO)(PPh_3)$	dtt		1603 [d]	1298, 1277				7·80
$IrH_2(tri)(PPh_3)_2$	dpt	2166 2142		1270		31·89	17·0	
	dtt	2122		1277, 1292		31·85	17·0	7·86
	dct	2142		1292, 1273		32·15	18·0	
	tmt	2156 2132		1294, 1285		31·80	17·0	
$IrHCl(tri)(PPh_3)_2$	dpt	2160		1280		33·53	14·25	
	dtt	2114		1295, 1284		33·5	14·0	
	dct	2142		1292, 1276		33·7	14·4	
$Pt(tri)_2(PPh_3)_2$	dpt			1310, 1281	1201			
	dtt			1308, 1283	1199			7·86
	dmt			1311, 1281	1200			
	dct			1290, 1274	1203			
	tmt			1311, 1279	1199			
$Pt(tri)_2(dppe)$	dtt			1311, 1282	1203			
$Pt(tri)_2(dppp)$	dtt			1313, 1279	1202			7·82
$Pt(tri)_2(dppb)$	dtt			1311, 1279	1195			
$PtCl(tri)(PPh_3)_2$	dtt			1309, 1282	1202			
	dmt			1309, 1290	1203			
	tmt			1309, 1283	1203			
$PtCl(tri)(PEt_3)_2$	dtt			1298, 1282	1203			
$Pd(tri)_2(PPh_3)_2$	dtt			1312, 1284	1205			7·78
	dmt			1312, 1286	1203			
	dct			1308, 1274	1208			
	tmt			1308, 1283	1200			
$Pd(tri)_2(dppp)$	dtt			1314, 1280	1202			

[a] For key to ligands see Table 1. [b] $\nu(\mathrm{tri})_1$ and $\nu(\mathrm{tri})_2$ main bands arising from triazene skeleton vibrations; other bands associated with 1,3-diaryltriazenido ligands appear at 1580—1600 and 1150 cm^{-1}. [c] N.m.r. spectra taken in $CDCl_3$ and referenced to internal tetramethylsilane. [d] ν(NO).

Palladium and Platinum Triazenido Complexes.—$M(ArNNNAr)_2(PPh_3)_2$. The zero oxidation state complexes $M(PPh_3)_4$ (M = Pd, Pt) react with 1,3-diaryltriazenes in cold benzene to afford complexes of stoicheiometry $M(ArNNNAr)_2(PPh_3)_2$, each of which exists in two isomeric forms. In our preliminary publications on this work we formulated these products as monodentate triazenido derivatives of square-planar palladium(II) and platinum(II),[9] and explained their temperature dependent ^1H n.m.r. spectra in terms of a rapid intramolecular triazenido ligand exchange process.[10] More recently Knoth [11] has suggested that our n.m.r. data are consistent with formulation of the complexes concerned as chelate triazenido derivatives of octahedral palladium(II) and platinum(II). Alternative octahedral [3] and square-planar [5] structures involving chelate and monodentate triazenido ligands respectively have also been proposed for the palladium(II) complexes $Pd(ArNNNAr)_2(py)_2$ and $Pd(ArNNNAr)_2(en)$ (en = $H_2NCH_2CH_2NH_2$) originally prepared by Dwyer.[3] However, six-co-ordination is uncommon for Pd^{II} and Pt^{II}, and we find no cause to revise our original conclusion that the complexes $M(ArNNNAr)_2L_2$ (M = Pd, Pt; L = PR_3, py, *etc.*) are square planar species containing monodentate triazenido ligands.

Irrespective of the overall co-ordination number ultimately assigned to the complexes $M(ArNNNAr)_2(PPh_3)_2$, the two forms of each complex, observed during this study, can be identified as *cis* and *trans* isomers on the basis of their solubility properties and the relative magnitudes of the couplings ^1J(PtP) observed in the ^{31}P n.m.r. spectra of the platinum derivatives (Table 3).[24] In each case the reaction product initially isolated was a *cis–trans* mixture, which slowly converted to pure *trans* form in the presence of free phosphine or triazene. The catalytic influence exerted by free ligand in this isomerisation process lends support to our formulation of the complexes concerned as square-planar rather than octahedral derivatives of palladium(II) and platinum(II).[25]

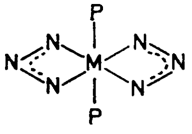
TABLE 3

^{31}P N.m.r. data [a] for 1,3-diaryltriazenido complexes of platinum and palladium

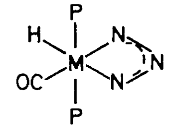
Complex [b]	δ [c]	^1J(PtP)	^2J(PP′)
cis-$Pt(dtt)_2(PPh_3)_2$	18·3	2870	
trans-$Pt(dtt)_2(PPh_3)_2$	−3·1	3364	
cis-$Pt(dmt)_2(PPh_3)_2$	18·47	2870	
trans-$Pt(dmt)_2(PPh_3)_2$	−2·94	3364	
trans-$Pt(dmt)(dtt)(PPh_3)_2$	−3·09	3360	
cis-$PtCl(dtt)(PPh_3)_2$	16·26	4007	17·8
	6·29	3037	
cis-$PtCl(dmt)(PPh_3)_2$	16·26	3989	17·9
	6·13	3037	
cis-$PtCl(tmt)(PPh_3)_2$	16·26	4013	17·9
	6·29	3037	
cis-$Pd(dtt)_2(PPh_3)_2$	23·54		
trans-$Pd(dtt)_2(PPh_3)_2$	19·12		
cis-$Pd(dmt)_2(PPh_3)_2$	23·54		
trans-$Pd(dmt)_2(PPh_3)_2$	19·29		
cis-$Pd(tmt)_2(PPh_3)_2$	23·54		
trans-$Pd(tmt)_2(PPh_3)_2$	19·12		

[a] Spectra recorded at 36·43 MHz in deuteriochloroform using solvent to provide ^2D field–frequency lock. All ^1H nuclei decoupled. [b] For key to ligands see Table 1. [c] Relative to external 85% H_3PO_4.

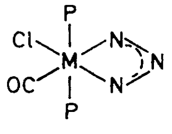
$M(ArNNNAr)_2[Ph_2P(CH_2)_nPPh_2]$ (n = 2—4). These complexes were obtained by reacting the chelate diphosphine derivatives $M[Ph_2P(CH_2)_nPPh_2]_2$ with triazenes in benzene. Their chemical and spectroscopic properties are similar to those recorded for the complexes *cis*-$M(ArNNNAr)_2(PPh_3)_2$ and they are accordingly assigned square-planar structures.



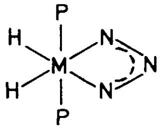
(I; M = Ru, Os)



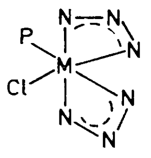
(II; M = Ru, Os)



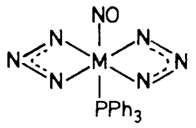
(III; M = Ru)



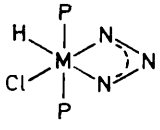
(IV; M = Rh, Ir)



(V; M = Rh)



(VI; M = Rh)



(VII; M = Ir)

In order to simplify these figures only the N–N–N skeletons of the 1,3-diaryltriazenido ligands are given.

$PtCl(ArNNNAr)(PR_3)_2$ (R = Ph, Et). The hydrides $PtClH(PR_3)_2$ react with 1,3-diaryltriazenes in boiling ethanol–benzene solution to afford complexes of stoicheiometry $PtCl(ArNNNAr)(PR_3)_2$. The triphenylphosphine derivatives are assigned as *cis* isomers of square-planar platinum(II) on the basis of their ^{31}P n.m.r. spectra (Table 3).

EXPERIMENTAL

Microanalyses were performed by Dr. Strauss at Oxford. I.r. spectra were recorded for Nujol mulls using Perkin-Elmer 457 and 621 grating spectrometers and were calibrated using polystyrene film. N.m.r. spectra were recorded in $CDCl_3$ solutions on Varian HA 100 or Bruker HFX 90 spectrometers and are referenced against internal tetramethylsilane. M.p.s were taken in air on a Kofler Hot Stage. Molecular weights were measured in benzene solution at 43° using a Perkin-Elmer–Hitachi vapour pressure osmometer.

[24] A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc.* (*A*), 1966, 1707.

[25] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967, p. 423.

Platinum metal salts were purchased from Johnson Matthey; hydrated ruthenium trichloride was used as purchased and may have contained appreciable amounts of ruthenium(IV) species.

The complexes $M[Ph_2P(CH_2)_nPPh_2]_2$ (M = Pd, Pt; n = 1—4) were prepared by the following general method: Potassium hydroxide (0·5 g) in ethanol–water (10 ml, 1 : 1 v/v) was added to a solution of the diphosphine (1·8 mmol) in ethanol (50 ml). The mixture was stirred and maintained at 70° while disodium tetrachloropalladate (0·24 g, 0·065 mmol) or disodium tetrachloroplatinate (0·25 g, 0·065 mmol) in water (10 ml) was added. The resultant yellow (platinum) or green (palladium) precipitate was filtered off, washed with ethanol, and dried *in vacuo*. Thus prepared were $Pt(Ph_2PCH_2CH_2PPh_2)_2$ (30%); $Pt(Ph_2PCH_2CH_2CH_2PPh_2)_2$ (84%); $Pt(Ph_2PCH_2CH_2CH_2CH_2PPh_2)_2$ (80%); $Pd(Ph_2PCH_2CH_2CH_2PPh_2)_2$ (52%). The complexes $RuHCl(PPh_3)_3$, $RhCl(PPh_3)_3$, $Pt(PPh_3)_4$, $PtHCl(PPh_3)_2$, and $Pd(PPh_3)_4$ were prepared by standard literature methods. Other platinum metal complexes were prepared by single-step syntheses developed by us.[12] The 1,3-diaryltriazenes were prepared by reaction of diazonium salts with primary amines under basic conditions, using the procedures described by Vogel.

Ruthenium Complexes

Bis(1,3-*diphenyltriazenido*)*bis*(*triphenylphosphine*)*ruthenium*(II).—*Method a. Single-stage preparation.* Warm solutions of ruthenium trichloride (0·13 g) in ethanol (10 ml), 1,3-diphenyltriazene (0·4 g) in ethanol (10 ml), and potassium hydroxide (0·2 g) in ethanol (5 ml) were added successively to a boiling solution of triphenylphosphine (0·54 g) in ethanol (10 ml), and the mixture heated under reflux for 2 min. After cooling the precipitate was washed with ethanol, water, and methanol to yield the required product as *red crystals* (47%). Purification was achieved by extraction of the sparingly soluble solid with dichloromethane, evaporation to small volume, and addition of methanol.

The following were similarly prepared: *bis*(1,3-*di*-p-*tolyltriazenido*)*bis*(*triphenylphosphine*)*ruthenium*(II) as red crystals (38%); *bis*[1,3-*di*(p-*methoxyphenyl*)*triazenido*]*bis*(*triphenylphosphine*)*ruthenium*(II) as red crystals (76%).

Method b. Using dihydridotetrakis(*triphenylphosphine*)-*ruthenium.* 1,3-Diphenyltriazene (0·38 g) and $RuH_2(PPh_3)_4$ (0·38 g) were heated together under reflux in 2-methoxyethanol (10 ml), with stirring, for 5 min. After cooling, the precipitate was washed with ethanol, water, and methanol to yield the required product as *red crystals* (89%).

The following were similarly prepared: *bis*(1,3-*di*-p-*tolyltriazenido*)*bis*(*triphenylphosphine*)*ruthenium*(II) as red crystals (89%); *bis*[1,3-*di*(p-*chlorophenyl*)*triazenido*]*bis*(*triphenylphosphine*)*ruthenium*(II) as red crystals (87%).

Method c. Using chlorohydridotris(*triphenylphosphine*)-*ruthenium.* 1,3-Di-*p*-tolyltriazene (0·4 g) and $RuHCl(PPh_3)_3$ (0·4 g) were heated together under reflux in ethanol (10 ml) for 30 min. After cooling the precipitate was washed with ethanol, water, and methanol to yield the required product as *red crystals* (40%).

Hydrido(1,3-*diphenyltriazenido*)*carbonylbis*(*triphenylphosphine*)*ruthenium*(II).—*Method a. Using dihydrido*(*carbonyl*)-*tris*(*triphenylphosphine*)*ruthenium.* (i) 1,3-Diphenyltriazene (0·2 g) in ethanol (10 ml) was added to a boiling solution of $RuH_2(CO)(PPh_3)_3$ (0·2 g) in benzene (10 ml) and the mixture heated under reflux for 20 min. Addition of methanol (20 ml) and cooling yielded a precipitate which was recrystallised from benzene–methanol as *red crystals* (92%) of the benzene adduct $RuH(PhNNNPh)(CO)(PPh_3)_2,C_6H_6$.

The following were similarly prepared: *hydrido*(1,3-*di*-p-*tolyltriazenido*)*carbonylbis*(*triphenylphosphine*)*ruthenium*(II) as orange crystals (94%); *hydrido*[1,3-*di*(p-*methoxyphenyl*)*triazenido*]*carbonylbis*(*triphenylphosphine*)*ruthenium*(II) as yellow crystals (89%); *hydrido*[1,3-*di*(p-*chlorophenyl*)*triazenido*]*carbonylbis*(*triphenylphosphine*)*ruthenium*(II) as yellow crystals (85%).

(ii) 1,3-Diphenyltriazene (0·2 g) and $RuH_2(CO)(PPh_3)_3$ were heated together under reflux in 2-methoxyethanol (10 ml) for 20 min. Dilution of the resultant solution with methanol (20 ml) yielded $RuH(PhNNNPh)(CO)(PPh_3)_2$ as *orange crystals* (95%).

Method b. Using chlorohydrido(*carbonyl*)*tris*(*triphenylphosphine*)*ruthenium.* 1,3-Diphenyltriazene (0·2 g) in ethanol (10 ml) was added to a boiling solution of $RuHCl(CO)(PPh_3)_3$ (0·2 g) in benzene (10 ml) and the mixture heated under reflux for 30 min. Addition of methanol (20 ml) and cooling yielded *red crystals* (98%) of the benzene adduct $RuH(PhNNNPh)(CO)(PPh_3)_2,C_6H_6$.

Similarly prepared was *hydrido*(1,3-*di*-p-*tolyltriazenido*)-*carbonylbis*(*triphenylphosphine*)*ruthenium*(II) as orange crystals (94%).

Method c. Using tricarbonylbis(*triphenylphosphine*)*ruthenium.* 1,3-Diphenyltriazene (0·3 g) and $Ru(CO)_3(PPh_3)_2$ (0·3 g) were heated together under reflux in 2-methoxyethanol (10 ml) for 1 h. Addition of methanol (30 ml) to the resultant solution yielded a precipitate which was recrystallised from dichloromethane–methanol as *orange-red crystals* (42%).

Chloro(1,3-*di*-p-*tolyltriazenido*)*carbonylbis*(*triphenylphosphine*)*ruthenium*(II)-*benzene*.—1,3-Di-*p*-tolyltriazene (0·05 g) and $RuHCl(CO)(PPh_3)_3$ (0·2 g) were shaken together in benzene (10 ml) for 12 h. Addition of methanol (20 ml) to the solution yielded a precipitate which was recrystallised from benzene–methanol as *green crystals* (58%).

The following were similarly prepared: *chloro*[1,3-*di*(p-*methoxyphenyl*)*triazenido*](*carbonyl*)*bis*(*triphenylphosphine*)-*ruthenium*(II)-*benzene* as green crystals (51%); *chloro*[1-p-*tolyl*-3-(p-*methoxyphenyl*)*triazenido*]*carbonylbis*(*triphenylphosphine*)*ruthenium*(II)-*benzene* as green crystals (51%).

Osmium Complexes

Bis(1,3-*diphenyltriazenido*)*bis*(*triphenylphosphine*)*osmium*(II).—Warm solutions of sodium chloro-osmate (0·28 g) in 2-methoxyethanol (10 ml), 1,3-diphenyltriazene (0·4 g) in 2-methoxyethanol (5 ml), and potassium hydroxide (0·2 g) in 2-methoxyethanol (5 ml) were added successively to a boiling solution of triphenylphosphine (0·54 g) in 2-methoxyethanol (10 ml) and the mixture heated under reflux for 5 min. The warm solution was filtered and the precipitate washed with ethanol, water, and methanol, and dried *in vacuo* as *dark green crystals* (39%).

The following were similarly prepared: *bis*(1,3-*di*-p-*tolyltriazenido*)*bis*(*triphenylphosphine*)*osmium*(II), recrystallised from benzene–methanol as green crystals (37%); *bis*(1,3-*di*-p-*chlorophenyltriazenido*)*bis*(*triphenylphosphine*)*osmium*(II) as green crystals (26%).

Hydrido(1,3-*di*-p-*tolyltriazenido*)*carbonylbis*(*triphenylphosphine*)*osmium*(II).—*Method a. Using chlorohydrido*(*carbonyl*)*tris*(*triphenylphosphine*)*osmium.* 1,3-Di-*p*-tolyltriazene (0·2 g) and $OsHCl(CO)(PPh_3)_3$ (0·2 g) were heated together under reflux in 2-methoxyethanol (10 ml) for 1 h. Addition of methanol (20 ml) and cooling gave a precipitate which was recrystallised from benzene–methanol as *yellow crystals* (65%).

The following were similarly prepared: *hydrido*[1,3-*di*(p-*methoxyphenyl*)*triazenido*]*carbonylbis*(*triphenylphosphine*)*osmium*(II) as yellow crystals (62%); *hydrido*[1,3-*di*(p-*chlorophenyl*)*triazenido*]*carbonylbis*(*triphenylphosphine*)*osmium*(II) as yellow crystals (81%).

Method b. Using dihydro(*carbonyl*)*tris*(*triphenylphosphine*)*osmium*. 1,3-Di-*p*-tolyltriazene (0·2 g) and $OsH_2(CO)(PPh_3)_3$ (0·2 g) were heated together under reflux in 2-methoxyethanol (10 ml) for 1 h. Addition of methanol and cooling gave a precipitate which was recrystallised from benzene–methanol as *yellow crystals* (78%).

The following were similarly prepared: *hydrido*[1,3-*di*(p-*methoxyphenyl*)*triazenido*]*carbonylbis*(*triphenylphosphine*)*osmium*(II) as yellow crystals (70%); *hydrido*[1,3-*di*(p-*chlorophenyl*)*triazenido*]*carbonylbis*(*triphenylphosphine*)*osmium*(II) as yellow crystals (71%).

Trihydrido(1,3-*diphenyltriazenido*)*bis*(*triphenylphosphine*)*osmium*(IV).—1,3-Diphenyltriazene (0·33 g) in benzene (5 ml) was added to a boiling solution of $OsH_4(PPh_3)_3$ (0·33 g) in 2-methoxyethanol (10 ml) and the mixture heated under reflux for 40 min. Addition of methanol (20 ml), and cooling, gave a precipitate which was recrystallised from dichloromethane–methanol *as brown crystals* (69%).

The following were similarly prepared: *trihydrido*(1,3-*di*-p-*tolyltriazenido*)*bis*(*triphenylphosphine*)*osmium*(IV) as green crystals (65%); *trihydrido*(1,3-*di*-p-*methoxyphenyltriazenido*)*bis*(*triphenylphosphine*)*osmium*(IV) as green crystals (57%); *trihydrido*(1,3-*di*-p-*chlorophenyltriazenido*)*bis*(*triphenylphosphine*)*osmium*(IV) as green crystals (80%); *trihydrido*(1-p-*tolyl*-3-p-*methoxyphenyltriazenido*)*bis*(*triphenylphosphine*)*osmium*(IV) as yellow crystals (62%).

Rhodium Complexes

Tris(1,3-*di*-p-*tolyltriazenido*)*rhodium*(III).— 1,3-Di-*p*-tolyltriazene (0·2 g) in ethanol (10 ml) and di-μ-chloro-bis(cycloocta-1,5-diene)dirhodium (0·3 g) in benzene (20 ml) were boiled together under reflux for 3 h; after 1 h and 2 h further 0·2 g portions of triazene were added. The resultant solution was evaporated to an oil, redissolved in dichloromethane, and chromatographed on silica gel. The orange fraction was collected, evaporated to small volume, then diluted with ethanol to give the required product as *orange crystals* (45%).

Dihydrido(1,3-*diphenyltriazenido*)*bis*(*triphenylphosphine*)*rhodium*(III).—*Method a. Single stage synthesis.* Warm solutions of rhodium trichloride (0·13 g) in ethanol (10 ml), 1,3-diphenyltriazene (0·2 g) in ethanol (5 ml), potassium hydroxide (0·2 g) in ethanol (5 ml) were added rapidly and successively to a boiling solution of triphenylphosphine (0·54 g) in ethanol (10 ml), and the mixture heated under reflux for 5 min. After cooling, the precipitate was washed with ethanol, water, and methanol, and dried *in vacuo* as *orange-red crystals* (78%).

Method b. Using hydridotetrakis(*triphenylphosphine*)*rhodium.* 1,3-Diphenyltriazene (0·38 g) and $RhH(PPh_3)_4$ (0·38 g) were heated together under reflux in ethanol (10 ml) for 10 min, with stirring. After cooling, the precipitate was washed with ethanol, water, and methanol, and dried *in vacuo* as *orange-red crystals* (80%).

The following were similarly prepared: *dihydrido*(1,3-*di*-p-*tolyltriazenido*)*bis*(*triphenylphosphine*)*rhodium*(III) as brown crystals (47%); *dihydrido*(1,3-*di*-p-*chlorophenyltriazenido*)*bis*(*triphenylphosphine*)*rhodium*(III) as green crystals (73%); *dihydrido*(1-p-*tolyl*-3-p-*methoxyphenyltriazenido*)*bistriphenylphosphine*)*rhodium*(III) as brown crystals (54%).

(1,3-*Diphenyltriazenido*)*carbonylbis*(*triphenylphosphine*)*rhodium*(I).—1,3-Diphenyltriazene (0·3 g) and $RhH(CO)(PPh_3)_3$ (0·3 g) were heated together under reflux in 2-methoxyethanol (10 ml) for 30 min. Addition of methanol (20 ml), and cooling, gave a precipitate which was recrystallised from benzene–methanol as *red crystals* (70%).

The following were similarly prepared: (1,3-*di*-p-*tolyltriazenido*)*carbonylbis*(*triphenylphosphine*)*rhodium*(I) as yellow crystals (77%); (1,3-*di*-p-*chlorophenyltriazenido*)*carbonylbis*(*triphenylphosphine*)*rhodium*(I) as yellow crystals (92%); (1-p-*tolyl*-3-p-*methoxyphenyltriazenido*)*carbonylbis*(*triphenylphosphine*)*rhodium*(I) as brown crystals (78%).

Chlorobis(1,3-*diphenyltriazenido*)(*triphenylphosphine*)*rhodium*(III)–½*benzene*.—1,3-Diphenyltriazene (0·5 g) and $RhCl(PPh_3)_3$ (0·5 g) were shaken together in benzene (10 ml) for 24 h. The solution was filtered, and, on standing at -5 °C for several days, the filtrate deposited the product as *orange-brown crystals* (71%).

The following were similarly prepared: *chlorobis*(1,3-*di*-p-*tolyltriazenido*)(*triphenylphosphine*)*rhodium*(III)–½*benzene* as red platelets (33%); *chlorobis*(1,3-*di*-p-*chlorophenyltriazenido*)(*triphenylphosphine*)*rhodium*(III)–½*benzene* as red crystals (77%).

Bis(1,3-*di*-p-*tolyltriazenido*)*nitrosyl*(*triphenylphosphine*)*rhodium*.—1,3-Di-p-tolyltriazene (0·4 g) and $Rh(NO)(PPh_3)_3$ (0·4 g) were shaken together in benzene (7 ml) for 1 h. Addition of methanol (30 ml) yielded the product as *dark red crystals* (86%).

Bis[*bis*(*diphenylphosphino*)*ethane*]*rhodium*(I) (1,3-*di*-p-*tolyltriazenide*).—Bis(diphenylphosphino)ethane (0·11 g) and $Rh(MeC_6H_4N{:}N{\cdot}NC_6H_4Me)(CO)(PPh_3)_2$ (0·1 g) were reacted together in benzene (5 ml). The solution cleared rapidly and precipitation began. After standing overnight, the product was washed with benzene as a *pale yellow solid* (60%).

Iridium Complexes

Dihydrido(1,3-*diphenyltriazenido*)*bis*(*triphenylphosphine*)*iridium*(III).—*Method a. Using trihydridotris*(*triphenylphosphine*)*iridium.* 1,3-Diphenyltriazene (0·2 g) in benzene (5 ml) was added to a boiling suspension of $IrH_3(PPh_3)_3$ (0·33 g) in 2-methoxyethanol (10 ml) and the mixture heated under reflux for 30 min. Addition of methanol (20 ml) and cooling yielded a precipitate which was recrystallised from benzene–methanol as *red crystals* (95%).

The following were similarly prepared: *dihydrido*(1,3-*di*-p-*tolyltriazenido*)*bis*(*triphenylphosphine*)*iridium*(III) as yellow crystals (80%); *dihydrido*(1,3-*di*-p-*chlorophenyltriazenido*)*bis*(*triphenylphosphine*)*iridium*(III) as yellow crystals (*ca.* 45%); *dihydrido*(1-p-*tolyl*-3-p-*methoxyphenyltriazenido*)*bis*(*triphenylphosphine*)*iridium*(III) as yellow crystals (*ca.* 50%).

Method b. Using hydrido(*carbonyl*)*tris*(*triphenylphosphine*)*iridium. Dihydrido*(1-p-*tolyl*-3-p-*methoxyphenyltriazenido*)*bis*(*triphenylphosphine*)*iridium*(III). 1-*p*-tolyl-3-*p*-methoxyphenyltriazene (0·2 g) and $IrH(CO)(PPh_3)_3$ (0·33 g) were heated together under reflux in benzene (8 ml) for 40 min. Addition of methanol (30 ml) and cooling yielded a precipitate which was recrystallised from benzene–methanol as *yellow crystals* (42%).

Method c. Single-stage preparation. Warm solutions of sodium chloroiridate (0·19 g) in 2-methoxyethanol (10 ml), 1,3-diphenyltriazene (0·2 g) in 2-methoxyethanol (5 ml), and potassium hydroxide (0·2 g) in 2-methoxyethanol (5 ml), were added successively to a boiling solution of triphenylphosphine (0·54 g) in 2-methoxyethanol (10 ml) and the mixture heated under reflux for 40 min. The solution was cooled and diluted with methanol–water to give a precipitate which was recrystallised from dichloromethane–methanol as *red crystals* (33%).

Chlorohydrido(1,3-diphenyltriazenido)bis(triphenylphosphine)iridium(III).—1,3-Diphenyltriazene (0·35 g) in benzene (5 ml) was added to a boiling solution of $IrHCl_2(PPh_3)_3$ (0·35 g) in 2-methoxyethanol (10 ml) and the mixture heated under reflux for 1 h. Addition of methanol (20 ml) and cooling yielded a precipitate which was recrystallised from benzene–methanol as *red crystals* (66%).

The following were similarly prepared: *chlorohydrido(1,3-di*-p-*tolyltriazenido)bis(triphenylphosphine)iridium*(III) as light brown crystals (53%); *chlorohydrido(1,3-di*-p-*chlorophenyltriazenido)bis(triphenylphosphine)iridium*(III) as yellow crystals (59%).

Platinum Complexes

cis- *and* trans-*Bis(1,3-di*-p-*tolyltriazenido)bis(triphenylphosphine)platinum*.—1,3-Di-*p*-tolyltriazene (0·3 g) and $Pt(PPh_3)_4$ (0·5 g) in benzene (5 ml) were shaken together for 1 h. The resultant yellow precipitate of benzene-solvated *cis*-bis(1,3-di-*p*-tolyltriazenido)bis(triphenylphosphine)platinum was filtered off and recrystallised from benzene–ethanol as solvent-free orange crystals (*ca.* 30%). The filtrate from the above reaction was allowed to stand for 24 h, then diluted with ethanol (15 ml) whereupon orange crystals (62%) of the *trans*-isomer slowly deposited.

cis- *and* trans-*Bis(1,3-di*-p-*methoxyphenyltriazenido)bis(triphenylphosphine)platinum*.—Similar treatment of $Pt(PPh_3)_4$ with 1,3-di-*p*-methoxyphenyltriazene gave a yellow precipitate (*ca.* 50%) of impure, benzene solvated, *cis*-bis(1,3-di-*p*-methoxyphenyltriazenido)bis(triphenylphosphine)platinum. Recrystallisation from benzene–ethanol gave pure non-solvated *cis*-isomer. The filtrate from the above reaction, set aside for 24 h then diluted with ethanol (15 ml), gave yellow crystals (47%) of the *trans*-isomer.

trans-*Bis(1*-p-*tolyl-3*-p-*methoxyphenyltriazenido)bis(triphenylphosphine)platinum*.—Similar treatment of $Pt(PPh_3)_4$ with 1-*p*-tolyl-3-*p*-methoxyphenyltriazene gave no *cis*-isomer; dilution of the benzene solution with ethanol after 24 h gave yellow crystals (84%) of *trans*-isomer.

Conversion of cis *to* trans *Form*.—*cis*-Bis(1,3-di-*p*-tolyltriazenido)bis(triphenylphosphine)platinum (0·25 g) dissolved in warm benzene (10 ml) was treated with 1,3-di-*p*-tolyltriazene (0·1 g) and allowed to stand for 24 h. Addition of ethanol, followed by concentration under reduced pressure gave substantially unchanged *cis*-isomer.

A similar experiment with triphenylphosphine (0·1 g) in place of the triazene gave complete conversion to *trans*-isomer after 3 days. In the presence of triphenylphosphine and the triazene, conversion to *trans*-isomer was complete within 24 h.

Bis(1,3-diphenyltriazenido)bis(triphenylphosphine)platinum(II).—1,3-Diphenyltriazene (0·4 g) and $Pt(PPh_3)_3$ (0·49 g) were shaken together in benzene (10 ml) for 12 h. The mixture was diluted with methanol (30 ml) and the required product was filtered off then recrystallised from benzene–methanol as red-orange crystals (58%).

Bis(1,3-di-p-*chlorophenyltriazenido)bis(triphenylphosphine)platinum*(II) was similarly prepared and was crystallised from benzene–methanol as yellow crystals (60%).

Bis(1,3-di-p-*tolyltriazenido)[bis(diphenylphosphino)ethane]platinum*(II).—1,3-Di-*p*-tolyltriazene (0·4 g) and $Pt(Ph_2PCH_2CH_2PPh_2)_2$ (0·5 g) were shaken together in benzene (10 ml) for 12 h. Addition of methanol (30 ml) yielded a precipitate of the required product, this was recrystallised from benzene–methanol as yellow crystals (48%). Similarly prepared were: *bis(1,3-di*-p-*tolyltriazenido)[bis(diphenylphosphino)propane]platinum*(II) as orange crystals (64%); *bis(1,3-di*-p-*tolyltriazenido)[bis(diphenylphosphino)butane]platinum*(II)*–benzene* as yellow crystals (95%).

cis-*Chloro(1,3-di*-p-*tolyltriazenido)bis(triphenylphosphine)platinum*(II).—1,3-Di-*p*-tolyltriazene (0·2 g) and $PtHCl(PPh_3)_2$ (0·35 g) in benzene (5 ml) were shaken together until the reactants dissolved. The solution was allowed to stand for 24 h then methanol (10 ml) was added and the required product was collected as orange crystals (71%). Similarly prepared were: cis-*chloro(1,3-di*-p-*methoxyphenyltriazenido)bis(triphenylphosphine)platinum*(II) as yellow crystals (75%); cis-*chloro-(1*-p-*tolyl-3*-p-*methoxyphenyltriazenido)bis(triphenylphosphine)platinum*(II) as yellow crystals (84%).

Chloro(1,3-di-p-*tolyltriazenido)bis(triethylphosphine)platinum*(II).—1,3-Di-*p*-tolyltriazene (0·15 g) and $PtHCl(PEt_3)_2$ were heated under reflux in methanol (8 ml) for 10 min. The solution was concentrated under vacuum to yield the required product as *orange crystals* (33%).

Palladium Complexes

cis *and* trans-*Bis(1,3-di*-p-*tolyltriazenido)bis(triphenylphosphine)palladium*(II).—1,3-Di-*p*-tolyltriazene (0·3 g) and $Pd(PPh_3)_4$ (0·5 g) were shaken together in benzene (5 ml), and formed a dark red solution within 5 min. Addition of ethanol (15 ml) at this stage gave pink microcrystals of *cis* and *trans* bis(1,3-di-*p*-tolyltriazenido)bis(triphenylphosphine)palladium (*ca.* 50 : 50). Yield 70%. If the deep red solution was allowed to stand for 24 h then diluted with methanol (10 ml) dark red crystals (76%) of almost pure *trans*-isomer were obtained.

Similarly prepared were: *bis(1,3-di*-p-*methoxyphenyltriazenido)bis(triphenylphosphine)palladium*(II) as red crystals (71%); *bis(1-p-tolyl-3-p-methoxyphenyltriazenido)bis(triphenylphosphine)palladium*(II) as red crystals (75%); *bis(1,3-di*-p-*chlorophenyltriazenido)bis(triphenylphosphine)palladium*(II) as orange crystals (69%); *bis(1,3-di*-p-*tolyltriazenido)[bis(diphenylphosphino)propane]palladium*(II)*–benzene* as brown crystals (33%).

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