1,3-Diaryltriazenido Derivatives of the Platinum Metals

By S. D. ROBINSON* and M. F. UTTLEY

(*Department of Chemistry, King's College, Strand, London* WC2R 2LS)

Summary Mononuclear triphenylphosphine complexes of the platinum metals containing monodentate and chelate 1,3-diaryltriazenido ligands are reported; complexes described include the first triazenido-metal hydride derivatives, and some non-rigid, seven-co-ordinate osmium(IV) trihydrides, $OsH_3(ArN\cdots N\cdots NAr)(PPh_3)_2$.

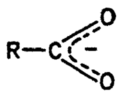
1,3-*Diaryltriazenido derivatives of the platinum metals*

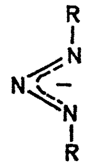
	Complex	Colour	ν(CO) cm^{-1}	ν(MH) cm^{-1}	τ (MH)	*J* (PH)/Hz	Precursor
(I)	$\mathrm{Pd(dtt)_2(PPh_3)_2}$[a]	red	—	—	—	—	$\mathrm{Pd(PPh_3)_4}$
(II)	$\mathrm{Pt(dtt)_2(PPh_3)_2}$	orange	—	—	—	—	$\mathrm{Pt(PPh_3)_3}$
(III)	$\mathrm{Rh(dpt)(CO)(PPh_3)_2}$[b]	orange	1952	—	—	—	$\mathrm{RhH(CO)(PPh_3)_3}$
(IV)	$\mathrm{RhH_2(dtt)(PPh_3)_2}$	red	—	2080, 2056 2036sh	27·35	15·5[c]	$\mathrm{RhH(PPh_3)_4}$
(V)	$\mathrm{IrHCl(dpt)(PPh_3)_2}$	red	—	2160	33·53	14·25 (t)[d]	α-$\mathrm{IrHCl_2(PPh_3)_3}$
(VI)	$\mathrm{IrH_2(dpt)(PPh_3)_2}$	red	—	2164, 2140	31·89	17·0 (t)	*mer*-$\mathrm{IrH_3(PPh_3)_3}$
(VII)	$\mathrm{RuCl(dtt)(CO)(PPh_3)_2}$	green	1926	—	—	—	$\mathrm{RuHCl(CO)(PPh_3)_3}$
(VIII)	$\mathrm{RuH(dpt)(CO)(PPh_3)_2}$	orange	1917	—	22·33	20·25 (t)	$\mathrm{RuH_2(CO)(PPh_3)_3}$
(IX)	$\mathrm{Ru(dpt)_2(PPh_3)_2}$	red	—	—	—	—	$\mathrm{RuH_2(PPh_3)_4}$
(X)	$\mathrm{OsH(dtt)(CO)(PPh_3)_2}$	yellow	1903	2002	22·85	18·5 (t)	$\mathrm{OsHCl(CO)(PPh_3)_3}$
(XI)	$\mathrm{OsH_3(dpt)(PPh_3)_2}$	brown	—	1910, 2100 2150sh	19·35	13·5 (t)	$\mathrm{OsH_4(PPh_3)_3}$

[a] dtt = 1,3-di-*p*-tolyltriazenido; [b] dpt = 1,3-diphenyltriazenido; [c] triplet of doublets [*J*(RhH)17·0 Hz]; [d] t = 1:2:1 triplet.

ALTHOUGH current studies of dinitrogen complexes have generated much interest in nitrogen donor ligands relatively little is known concerning 1,3-diaryltriazenido complexes of the transition metals. Most of the examples previously reported are thought to be triazenido bridged dimers[1,2] and only one structure involving chelate triazenido ligands has been rigorously established.† The close structural analogy[1] between carboxylate anions (I), the ligand properties of which have been widely studied, and 1,3-diaryltriazenido anions (II), prompted the present investigation in which an extensive series of platinum-metal complexes, containing monodentate and chelate 1,3-diaryltriazenido ligands has been synthesised.

The triazenido derivatives are readily prepared by treating triphenylphosphine complexes of the platinum metals with the appropriate 1,3-diaryltriazen in benzene or an alcoholic solvent. A selection of the complexes prepared in this way, together with their precursors is listed in the Table; related derivatives of 1,3-di-*p*-anisyl- and 1,3-di-*p*-chlorophenyl-triazens have also been isolated. All the complexes are diamagnetic, highly coloured, crystalline solids; all are monomeric (benzene 44°) and give excellent analytical data [C, H, N, P, (Cl)]. Unlike some previously reported[4] diphenyltriazenido complexes our products are air stable and do not readily undergo hydrolysis.


(I)


(II)

The mode of co-ordination of the 1,3-diaryltriazenido ligand may be deduced with the aid of i.r. data. Complexes (IV)—(X), which may reasonably be expected to adopt six-co-ordinate structures and thus contain chelate triazenido ligands, show i.r. bands at *ca.* 1260—1300 and 1580—1600 cm^{-1}. In contrast, complexes (I)—(III) have i.r. spectra with bands at *ca.* 1150, 1190—1210, 1260—1300, and 1580—1600 cm^{-1}, and are therefore tentatively assigned square-planar four-co-ordinate structures with monodentate triazenido ligands.

The osmium derivatives, $\mathrm{OsH_3(ArN{\cdots}N{\cdots}NAr)(PPh_3)_2}$ (type XI; Ar = phenyl, *p*-tolyl, *p*-anisyl, *p*-chlorophenyl) show i.r. bands consistent with the presence of chelate triazenido ligands and are, therefore, presumably seven-co-ordinate. Careful integration of signals in the n.m.r. spectra of the di-*p*-tolyl- and di-*p*-anisyl triazen derivatives, arising from the aryl, methyl, and hydridic protons, confirms the trihydride formulation (XI) for these complexes. Moreover their high-field ^{1}H n.m.r. spectra comprise a well-defined 1:2:1 triplet, compatible with the presence of a non-rigid, seven-co-ordinate structure. Similar n.m.r. data have recently been reported for the related, non-rigid, heptaco-ordinate osmium(IV) hydrides, $\mathrm{OsH_4(PR_3)_3}$,[5,6] $\mathrm{OsH_2Cl_2(PR_3)_3}$,[7] and $\mathrm{OsHCl_3(PR_3)_3}$[7] [R = alkyl, aryl].

We suggest that the triazenido complexes reported here adopt monomeric structures with chelate or monodentate triazenido ligands, rather than the more usual dimeric arrangements, in order to minimise intramolecular steric interactions between the bulky aryl groups of the ligands present.

Preliminary studies indicate that under suitable conditions 1,3-diaryltriazens will also react with platinum metal halides in the presence of triarylphosphines to afford arylazo ($\mathrm{ArN_2}$) derivatives.[8]

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† The complex $\mathrm{Co(PhN{\cdots}N{\cdots}NPh)_3}$ has been shown by *X*-ray diffraction studies[3] to possess a tris-chelate structure; the related iron(III) derivative is monomeric and probably has a similar structure.[4]

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