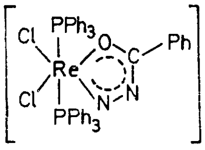
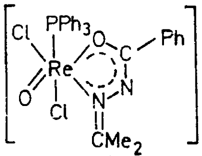
Anomalous Hydrogen-1 and Carbon-13 Spectra of some New *N*-Acyl-*N*′-aryldiazene Complexes of Osmium

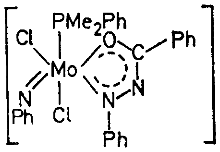
By **Joseph Chatt, Jonathan R. Dilworth,*** and **Takashi Ito,** A.R.C. Unit of Nitrogen Fixation, University of Sussex, Brighton BN1 9QJ

The complex $[OsCl_3O(PPh_3)_2]$ reacts with the hydrazides $4-RC_6H_4NHNHCOR'$ (R = MeO, Me, H, Cl, or NO_2; R′ = H, Me, Et, Pr^n, Bu^t, or CH_2Ph) to give the *N*-acyl-*N*′-aryldiazene complexes $[OsCl_2(4-RC_6H_4{\cdot}N_2{\cdot}COR')(PPh_3)_2]$. Although apparently diamagnetic, their ^1H and ^{13}C n.m.r. spectra show shifts of a pattern and magnitude characteristic of paramagnetic species. Moreover these shifts are restricted to certain protons and carbon atoms of the diazene ligand, and the tertiary phosphine protons and carbon atoms show no anomalies. The magnitude of the shifts is highly dependent on the nature of the substituents in the diazene *N*-phenyl group, and there is an approximately linear relation between the shifts and Hammett σ constants for the substituent. Variable-temperature ^1H n.m.r. spectra suggest that a second-order paramagnetic effect may be responsible for the shifts.

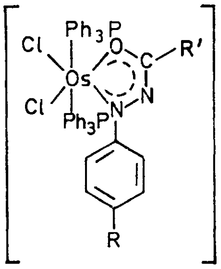
OUR earlier investigations of the reactions of metal oxo-complexes with substituted hydrazines[1,2] have shown that complexes of structures (A) and (B) were obtained from $[ReCl_3O(PPh_3)_2]$ and benzoylhydrazide hydrochloride in ethanol [structure (A)] or acetone [structure (B)]. The complex $[MoCl_2O(PMe_2Ph)_3]$ reacts with *N*′-aryl- or *N*′-alkyl-aroylhydrazides to give complexes of structure (C),[2] whereas $[ReCl_3O(PPh_3)_2]$ reacts to give the arylimido-derivatives $[ReCl_3(NAr)(PPh_3)_2]$.[1] The complex $[OsCl_3O(PPh_3)_2]$ reacts with hydrazine dihydrochloride to give $[OsCl_3(NH_3)(PPh_3)_2]$.[3]


(A)


(B)


(C)

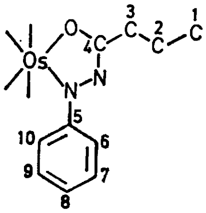
In this paper we describe the preparation of substituted diazene complexes of osmium, $[OsCl_2(RC_6H_4{\cdot}N_2{\cdot}COR')(PPh_3)_2]$, (I), by reaction of $[OsCl_3O(PPh_3)_2]$ with *N*′-arylacylhydrazides in refluxing ethanol in the presence of triphenylphosphine.[4] The complexes are of general structure (D), confirmed for the derivative with R = H and R′ = Me by *X*-ray crystallography,[5] and a series with different R and R′ groups (Table 1) were obtained using the appropriate hydrazides.


(D)

RESULTS AND DISCUSSION

The dibromo-analogue $[OsBr_2(Ph{\cdot}N_2{\cdot}COMe)(PPh_3)_2]$, (II), was prepared from $[OsBr_3O(PPh_3)_2]$. Complexes with other tertiary phosphines, (III), (V), and (VI), or trimethyl phosphite, (IV), as ligands were prepared by ligand exchange from the triphenylphosphine complexes, (I). The dithiocarbamato-complexes [(VII) and (VIII), Table 2] were obtained by treating (I) with an excess of the appropriate sodium dithiocarbamate in methanol or acetone under reflux. Some substituted *N*′-phenylacylhydrazides, *e.g.* $2,5-Cl_2C_6H_3NHNHCOMe$ gave the hydride $[OsHCl_3(PPh_3)_3]$ instead of complexes of structure (D). The hydrazide $4-O_2NC_6H_4NHNHCOMe$ yielded a mixture of the hydride and a complex of type (D), whereas reaction of the amine $PhCOCH_2NHPh$ with $[OsCl_3O(PPh_3)_2]$ also yielded the hydride.

I.r. and U.v. Spectra.—Bands due to ν(N–H) and ν(C=O) occur at 3 200—3 300 and 1 650 cm⁻¹ respectively in the i.r. spectra of the parent hydrazines but were absent from those of the complexes, in accord with structure (D). The stretching frequency ν(Os-Cl) appeared generally at *ca.* 290 cm⁻¹ in the far-i.r. spectra (see Table 1) as a broad band, resolved into a doublet in some cases. This band was absent from the spectra of the bromo-analogues, but ν(Os-Br) was not visible.



(E)

The u.v. solution spectra of the complexes (Table 1) showed intense absorptions at *ca.* 230, 260, 400, and 500 nm. The ε values suggest that all arise from charge-transfer transitions. The last three absorptions depended markedly on the nature of the substituents on the chelate ring; however, no correlation between this dependence and the anomalous ^1H and ^{13}C n.m.r. spectra (see below) could be made.

^1H N.M.R. Spectra.—In the following discussion the carbon atoms of the diazene-ring system are numbered as

---

[1] J. Chatt, J. R. Dilworth, G. J. Leigh, and V. D. Gupta, *J. Chem. Soc.* (*A*), 1971, 2631.

[2] J. Chatt and J. R. Dilworth, *J.C.S. Chem. Comm.*, 1972, 549.

[3] J. Chatt, C. D. Falk, G. J. Leigh, and R. J. Paske, *J. Chem. Soc.* (*A*), 1969, 2288.

[4] J. Chatt, J. R. Dilworth, and T. Ito, *J.C.S. Chem. Comm.*, 1973, 77.

[5] M. B. Hursthouse, personal communication.

TABLE 1

Complexes $[OsCl_2(RC_6H_4{\cdot}N_2{\cdot}COR')(PPh_3)_2]$, (I), $[OsBr_2(Ph{\cdot}N_2{\cdot}COMe)(PPh_3)_2]$, (II), $[OsCl_2(Ph{\cdot}N_2{\cdot}COR')(PMePh_2)_2]$, (III), $[OsCl_2(Ph{\cdot}N_2{\cdot}COMe)\{P(OMe)_3\}]$, (IV), $[OsCl_2(Ph{\cdot}N_2{\cdot}COCH_2Ph)(PMe_2Ph)_2]$, (V), and $[OsCl_2(Ph{\cdot}N_2{\cdot}COCH_2Ph)(PEt_3)_2]$, (VI)

Complex	R	R′	Appearance	Yield [a] %	M.p. (decomp.) (θ_c/°C)	Analysis/% [b] C	H	N	*M* [b]	ν(Os–Cl) [c] cm^{-1}	Electronic spectra (nm) [d]			
(I)	4-MeO	Me	Brick-red fine needles	91	157—160	55.5 (56.1)	4.1 (4.2)	3.0 (2.9)	905 (978)	282	232 (39 300)	257 (33 000)	413 (7 830)	484 (10 490)
(I)	4-MeO	Et	Brick-red fine needles	84	160—161	56.2 (56.5)	4.5 (4.3)	2.9 (2.9)		273	233 (40 900)	261 (33 300)	410 (6 730	502 (10 900)
(I)	4-MeO	H	Deep brown prisms	75	168—171	56.1 (56.6)	4.3 (4.1)	3.1 (3.0)		297	233 (43 855)	255 (34 440)	413 (10 850)	490 (6 615)
(I)	4-MeO	Me	Brown needles	67	189—194	56.9 (57.0)	4.6 (4.3)	3.0 (3.0) [e]	940 (948)	293	232 (39 000)	256 (30 700)	403 (7 470)	483 (5 600)
(I)	3-MeO	Et	Brown fine needles	85	164—168	57.3 (57.4)	4.4 (4.4)	2.9 (2.9)	910 (962)	274	232 (40 200)	259 (32 000)	410 (8 560)	490 (5 960)
(I)	3-MeO	Me	Brown needles	51	175—179	57.3 (57.0)	4.1 (4.3)	3.1 (3.0)		288				
(I)	H	H	Brown needles	43	174—177	55.2 (55.2) [f]	4.0 (3.9) [f]	2.9 (3.0) [f]		301	233 (43 070)	257 (30 870)	406 (6 175)	485 (4 433)
(I)	H	Me	Bright brown needles	34	177—181	56.3 (56.6)	4.2 (4.1)	3.2 (3.0) [g]	950 (934)	294				
(II)	H	Me	Brown needles	100	169—170	51.0 (51.7)	3.7 (3.7)	2.8 (2.7)						
(III)	H	Me	Light brown prisms	52	179—181	50.8 (50.4)	4.6 (4.2)	3.4 (3.5)		293				
(IV)	H	Me	Dark brown prisms	53	92—97	25.9 (25.6)	4.1 (4.0)	4.2 (4.3)		325, 321				
(I)	H	Et	Dark brown needles	57	171—175	56.0 (57.0)	4.2 (4.3)	2.8 (3.0)		292	233 (47 500)	257 (31 000)	395 (6 970)	470 (5 440)
(I)	H	Pr^n	Bright brown needles	82	186—189	57.6 (57.4)	4.6 (4.4)	3.1 (2.9)	880 (962)	291	233 (42 610)	261 (30 750)	406 (8 220)	490 (6 130)
(I)	H	Bu^t	Brown needles	86	180—185	57.5 (57.8)	4.8 (4.5)	3.0 (2.9)	975 (976)	284	232 (40 390)	250 (29 010)	407 (8 415)	490 (6 130
(I)	H	PhCH$_2$	Brown prisms	84	181—183	59.2 (59.5)	4.3 (4.2)	3.0 (2.8)		293				
(III)	H	PhCH$_2$	Brown prisms	72	166—167	54.7 (54.2)	4.4 (4.3)	3.3 (3.2)		295, 284				
(V)	H	PhCH$_2$	Brown prisms	84	161—171	48.5 (47.3)	4.7 (4.5)	3.9 (3.7)		298, 283				
(VI)	H	PhCH$_2$	Deep brown prisms	21	87—88	44.4 (43.3)	5.9 (5.9)	4.0 (3.9)						
(I)	4-Cl	Me	Brick-red fine needles	82	175—179	56.9 (57.2)	4.2 (4.1)	2.5 (2.7)		279	233 (39 630)	258 (26 530)	406 (6 230)	494 (4 155)
(I)	4-Cl	Et	Brick-red fine needles	85	171—172	54.9 (55.0)	4.4 (4.0)	2.8 (2.9)		278				
(I)	4-O$_2$N	Me	Dark brown needles	74	172—180	57.6 (54.0)	4.2 (3.8)	3.6 (4.3)		302				
(I)	4-O$_2$N	Et	Brown needles	82	171—174	54.3 (54.4)	4.2 (4.0)	3.9 (4.2)		293	233 (51 100)	263 (31 000)	385 (11 600)	520 (4 580)

[a] Based on $[OsCl_3O(PPh_3)_2]$. [b] Calculated values are given in parentheses. [c] In Nujol mulls. [d] In dichloromethane solution. Molar absorption coefficients (ϵ/l mol^{-1} cm^{-1}) are given in parentheses. [e] P, 6.4 (6.5); Cl, 7.3 (7.5%). [f] Calculated values are those for the $\frac{1}{2}CH_2Cl_2$ adduct. [g] P, 6.8 (6.6); Cl, 7.6 (7.6%). [h] P, 6.5 (6.3); Cl, 7.7 (10.8%).

shown in (E); H^6 then refers to the proton attached to carbon C^6, H^3 to that on C^3, *etc.* Since oxidation to the corresponding diazene-compounds causes no significant change in the chemical shifts of the substituent groups, the hydrazide chemical shifts are taken to represent the unco-ordinated diazene-compounds. The large differences in shifts between the hydrazide and corresponding diazene complex must occur on co-ordination of the diazene molecule.

^1H N.m.r. spectra of complexes (I; R′ = Et) are shown in Figure 1 and data for other complexes summarised in Table 2. The greatest shifts (relative to the free hydrazides) occurred for the H^3, H^7, and H^9 protons (downfield) and the H^6, H^{10}, and H^8 protons (upfield). Much smaller shifts were observed for the H^4 (upfield) and H^1 and H^2 protons (downfield) (Table 2). The observed shift pattern, particularly the alteration in sign of the shift of the protons of the Ph group attached to the chelate ring, is characteristic of delocalisation of unpaired electron density in a π system. Another criterion of π delocalisation was observed; *viz.* replacement of a proton by a Me group caused the Me protons to shift in the opposite sense to the replaced proton. Thus H^4 and H^3 in complexes (I; R = H, R′ = H and Me), H^8 and 4-Me in (I; R = H, R′ = Me) and (I; R = 4-Me, R′ = Et), and H^7 and 4-Me in complexes (I; R = H, R′ = Me) and (I; R = 4-Me, R′ = Me) showed shifts in opposite senses. However, along the R′ group alkyl chain, replacement of H by Me did not change the sign of the shifts since π delocalisation cannot operate there.

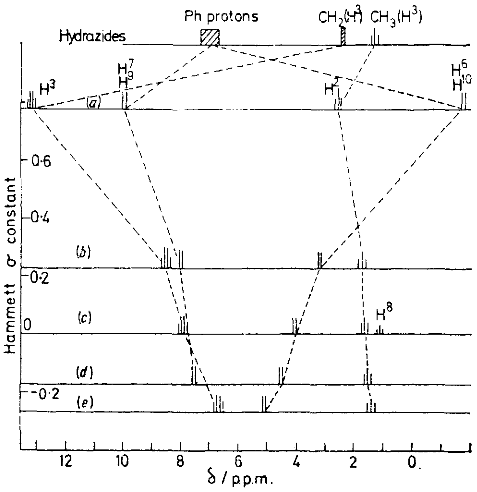


FIGURE 1 Correlation diagram for ^1H chemical shifts of the hydrazides $4\text{-}RC_6H_4NHNHCOEt$ and the complexes $[OsCl_2(4\text{-}RC_6H_4{\cdot}N_2{\cdot}COEt)(PPh_3)_2]$ as functions of the Hammett σ constants for R = NO_2 (*a*), Cl (*b*), H (*c*), Me (*d*), and MeO (*e*)

As Figure 1 shows, shifts of H^3, H^6, and H^{10} are not only large but approximately linearly dependent on the

Hammett σ constants[6] for the substituent R. This suggests that there is a high degree of delocalisation over the chelated diazene-ring system, in agreement with the *X*-ray crystal structure[5] which shows the diazene Ph group to be coplanar with the N–N–C(R′)–O system.

TABLE 2

^{1}H N.m.r. spectra of the complexes (I)—(VI), $[Os(S_2CNMe_2)_2(RC_6H_4{\cdot}N_2{\cdot}COMe)]$, (VII), $[Os(S_2CNEt_2)_2(4\text{-}O_2NC_6H_4{\cdot}N_2{\cdot}COMe)]$, (VII), and the corresponding hydrazides $4\text{-}RC_6H_4NHNHCOR'$ (in square brackets)

			δ[a] p.p.m.						
			R′ Protons			*N*-Phenyl protons[b]			
Complex	R	R′	H^1 or H^4	H^3	H^2	H^6 and H^{10}	H^7 and H^9	H^8	R
(I)	H	H	0.34 (s) [1.29 (m)]			2.84 (d)	8.16 (t)	−0.39 (t)	
(I)	4-MeO	Me		6.29 (s) [2.16 (s)]		5.04 (d)	7.2		4.03 (s) [3.78 (s)]
(I)	4-Me	Me		6.92 (s) [2.09 (s)]		4.54 (d)	7.66 (d)		5.73 (s) [2.30 (s)]
(I)	H	Me		7.58 (s) [2.11 (s)]		4.06 (d)	7.91 (t)	0.98 (t)	
(I)	4-Cl	Me		9.27 (s) [2.12 (s)]		3.38 (d)	8.08		
(I)	4-O_2N	Me		12.57 (s) [c]		1.08 (d)	10.00 (d)		
(I)	4-MeO	Et		6.62 (q) [2.37 (m)	1.43 (t) [1.21 (b)]	5.03 (d)	obs.		4.06 (s) [3.82 (s)]
(I)	4-Me	Et		obs. [2.38 (m)]	1.50 (t) [1.23 (t)]	4.44 (d)	7.57 (d)		5.78 (s) [2.31 (s)]
(I)	H	Et		7.90 (q) [2.30 (m)]	1.60 (t) [1.23 (t)]	3.95 (d)	obs.	1.11 (t)	
(I)	4-Cl	Et		8.54 (q) [2.35 (m)]	1.73 (t) [1.25 (t)]	3.16 (d)	8.05 (d)		
(I)	4-O_2N	Et		13.05 (q) [2.36 (m)]	2.56 (t) [1.29 (t)]	−1.90 (d)	9.95 (d)		
(I)	H	Pr^n	1.23 (t) [0.96 (t)] [d]	7.49 (t) [2.32 (m)]	2.08 (sx) [1.71 (sx)]	3.90 (d)	7.88 (t)	1.03 (t)	
(I)	H	Bu^t			2.00 (s) [1.23 (s)]	3.60 (d)	7.81 (t)	0.59 (t)	
(I)	H	$PhCH_2$		7.46 (s) [3.78 (s)]		4.14 (d)	7.81 (t)	1.47 (t)	
(III)	H	$PhCH_2$		6.49 (s) [3.78 (s)]		5.38 (d)	7.63 (t)	3.48 (t)	
(V)	H	$PhCH_2$		6.05 (s) [3.78 (s)]		5.46 (d)	obs.	3.82 (t)	
(VI)	H	$PhCH_2$		8.40 (s) [3.78 (s)]		5.03 (d)	8.37 (t)	2.62 (t)	
(I)	3-Me	Me		7.54 (s) [2.12 (s)]		4.08 (s), 4.24 (d)	7.96 (t)	2.10 (d)	0.83 (s) [2.34 (s)]
(II)	H	Me		obs. [2.11 (s)]		4.78	7.95 (t)	1.74 (t)	
(III)	H	Me		6.10 (s) [2.11 (s)]		5.36 (d)	7.58 (t)	3.23 (t)	
(IV)	H	Me		3.42 (s) [2.11 (s)]		obs.	obs.	obs.	
(VII)	H	Me		4.35 (s) [2.11 (s)]		7.10 (d)	7.40 (t)	6.57 (t)	
(VII)	4-O_2N	Me		4.71 (s) [c]		6.65 (d)	8.31 (d)		
(VIII)	4-O_2N	Me		4.65 (s) [c]		6.70 (d)	8.31 (d)		

[a] In $CDCl_3$ solution at room temperature and 100 MHz (see text for notation); phosphine resonances have been omitted; s = singlet, d = doublet, t = triplet, q = quartet, sx = sextuplet, obs. = resonance obscured. [b] Protons H_{6-10} occurred as unresolved multiplets in the region 6—7 p.p.m. for the hydrazides. [c] Too insoluble. [d] H^1 protons.

X-Ray photoelectron (*X*-p.e.) spectra of complexes (I; R = 4-MeO and 4-O_2N, R′ = Me) showed that variation of substituent R caused significant differences in the osmium 4*f* level binding energies, *e.g.* 54.6 (R = 4-MeO) and 55.9 eV (R = 4-O_2N).* The 1.3 eV difference suggests considerable participation of the osmium atom in electron delocalisation over the diazene-ring system. There were no detectable differences in the binding energies of the diazene-nitrogen atoms or of the chlorine or phosphorus atoms.

The chemical shifts of H^3 were also dependent on the tertiary phosphine ligands. Generally the more aliphatic the phosphine the greater the upfield shift of the protons. The chemical shifts of protons in the tertiary phosphine ligands themselves are summarised in Table 3 and are normal for diamagnetic osmium complexes. Thus for complexes (III; R = H, R′ = Me and CH_2Ph) with $PMePh_2$ the Me protons were observed as 1 : 2 : 1 triplets at *ca.* 1.8 p.p.m. (*cf.* 2.08 p.p.m. for $[OsCl_2(CO)_2(PMePh_2)_2]$[7]), also confirming that the two

---

* 1 eV ≈ 1.60×10^{-19} J, 1 B.M. ≈ 9.27×10^{-24} Am^2.

[6] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420.

[7] D. P. Melville, D.Phil. Thesis, University of Sussex, 1970, p. 71.

phosphine ligands are mutually *trans*. The Me protons of the PMe_2Ph ligand in complex (V) appeared as a pair of asymmetric triplets centred at 1.37 and 1.12 p.p.m. due to the asymmetry of the complex. These spectra are in contrast to those of tertiary phosphine complexes with first- or second-order paramagnetism where the phosphine protons show large anomalous shifts.

TABLE 3

^1H N.m.r. spectra of the tertiary phosphine ligands in the complexes $[OsCl_2(Ph'\cdot N_2\cdot COR')L_2]$ in $CDCl_3$ solution at room temperature at 100 MHz

Complex	R′	L	δ/p.p.m.	Assignment
(III)	Me	$PMePh_2$	1.80 (t)	Me (H)
			7.75 (m)	*o*-, *m*-, *p*-H
(IV)	Me	$P(OMe)_3$	3.85 (d)	Me
			3.75 (d)	
(III)	$PhCH_2$	$PMePh_2$	1.76 (t)	Me (H)
			7—7.3 (m)	*o*-, *m*-, *p*-H
(V)	$PhCH_2$	PMe_2Ph	1.12 (t)	Me
			1.37 (t)	
			7—7.3 (m)	*o*-, *m*-, *p*-H
(VI)	$PhCH_2$	PEt_3	0.73 (q)	Me (H)
			1.13 (m)	CH_2 (H)

The $P(OMe)_3$ complex (IV) showed Me resonances as pairs of asymmetric doublets, suggesting that in this case the phosphite ligands are mutually *cis*. This change in configuration markedly reduces the shifts of the chelated diazene-protons compared to the *trans* complexes. There were no abnormalities in the chemical shifts of the diazene Ph group, suggesting that the change in configuration causes the Ph ring to twist out of the plane of the diazene-ring disrupting delocalisation. A similar effect was observed in the ^1H n.m.r. spectra of complexes $[Os(4\text{-}RC_6H_4\cdot N_2\cdot COR')(S_2CNR''_2)]$ [(VII) and (VIII), Table 2] where the diazene Ph-group resonances showed no abnormalities and the chemical shifts of the R′ alkyl group were only *ca.* 2 p.p.m. downfield from those of the hydrazide. Moreover, the chemical shift of R′ was independent of the substituent R suggesting that the diazene Ph group has again rotated out of the plane of the diazene-ring system.

The observed anomalous ^1H shifts were independent of field strength, being the same at 60 and 100 mHz. However, they were proportional to the absolute temperature (Figure 2) which suggests that the shifts are not the result of first-order paramagnetism, but some second-order effect. First-order paramagnetism frequently gives rise to large chemical shifts, but these depend inversely on temperature. Large chemical shifts arising from a second-order Zeeman effect have been reported for rhenium(III) and osmium(IV) complexes,[8] which have measurable temperature-independent susceptibilities, with magnetic moments of *ca.* 2.0 B.M. However, the osmium diazene complexes appear to be diamagnetic, by conventional Faraday measurements at 298 and 100 K, and in solution by the n.m.r. method. They also failed to show any significant e.s.r. spectra over the temperature range 12—298 K. The very weak signals observed were 10^3—10^4 times less intense than those normally encountered for paramagnetic complexes.

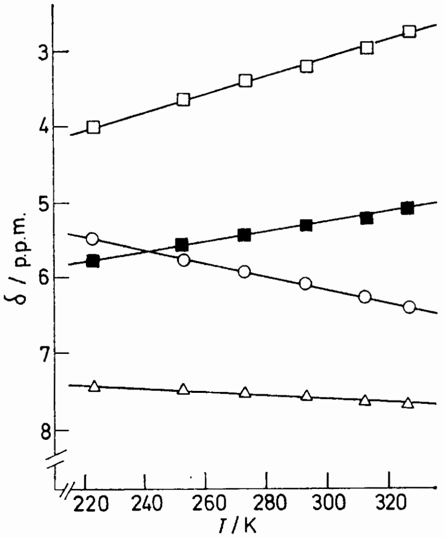


FIGURE 2 Temperature dependence of ^1H chemical shifts for the complex $[OsCl_2(Ph\cdot N_2\cdot COMe)(PMe_2Ph_2)_2]$: H^8 (□), H^3 (Me) (○), H^6 and H^{10} (■), and H^7 and H^9 (△)

TABLE 4

^{13}C Chemical shifts (p.p.m.) [a] for complexes (I; R′ = Et) and the hydrazides $4\text{-}RC_6H_4NHNHCOEt$

Compound	C^2	C^3	C^4	C^6,C^{10}	C^7,C^9	C^8
Hydrazide [b]	9.6	27.6	173.8	114.7 ± 1		
$R = NO_2$	28.6	1.5	258.0	70.0	206.0	
R = Cl	21.8	10.0		99.5	174.0	
R = H	20.7	11.1	262.1	104.5	167.0	159.7
R = MeO	18.8	13.8		94.7	160.7	

[a] In $CDCl_3$, downfield positive; carbon atoms numbered as in (E). [b] Resonances almost invariant with R.

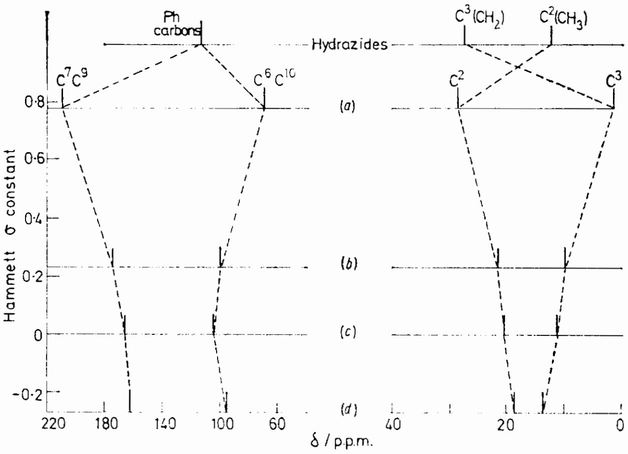


FIGURE 3 Correlation diagram for ^{13}C chemical shifts of the hydrazides $4\text{-}RC_6H_4NHNHCOEt$ and the complexes $[OsCl_2(4\text{-}RC_6H_4\cdot N_2\cdot COEt)(PPh_3)_2]$ as functions of Hammett σ constants for $R = NO_2$ (*a*), Cl (*b*), H (*c*), and MeO (*d*)

^{13}C *N.M.R. Spectra*.—^{13}C N.m.r. spectra of complexes (I; R′ = Et) are summarised in Table 4 and represented as a function of the Hammett σ constant for R in Figure 3. Assignment of resonances due to the non-tertiary carbon atoms of the diazene ring-system was achieved

---

[8] J. Chatt, G. J. Leigh, and D. M. P. Mingos, *J. Chem. Soc.* (*A*), 1969, 1674.

using single-frequency off-resonance decoupling or interrupted ^{1}H decoupling. Generally, resonances due to the tertiary carbon atoms were either too weak to be observed or their assignments could not be confirmed.

In the off-resonance decoupled ^{13}C spectrum of (I; R = H, R′ = Et) carbon atoms C^{2} and C^{3} (Me and CH_2 respectively) appeared as a quartet and a triplet. Atoms C^{7}, C^{9}, and C^{8} gave rise to triplets, and C^{6} and C^{10} to a doublet. The position of the resonance due to C^{4} was confirmed by comparison with the ^{13}C offset resonance-decoupled spectrum of (I; R = R′ = H) (Table 1), where a peak at 241 p.p.m. appeared as a doublet due to coupling with the formyl proton. Although only small downfield shifts were observed for the H^{2} [Me, see (E)], the C^{2} carbon atoms showed quite large downfield shifts of up to 19 p.p.m., and their magnitude was very dependent on R (Figure 1). The C^{3} resonances appeared upfield relative to the hydrazide in contrast to H^{3} which shifted downfield. The ^{13}C shifts of C^{7} and C^{9} showed an approximately linear dependence on the Hammett σ constant for R, but C^{6} and C^{10} showed an apparent anomaly for R = 4-MeO the value being 15 p.p.m. less than that required for an approximately linear dependence.

Table 5 summarises the relative magnitudes and signs of the ^{1}H and ^{13}C chemical shifts relative to the hydrazide. The C^{2} carbon atoms showed quite large shifts relative to H^{2} which is compatible with the diminution in shift magnitude anticipated for σ propagation of unpaired electron density along the alkyl chain. Shifts of C^{6}, C^{10} and C^{7}, C^{9} were of the same sign as H^{6}, H^{10}, and H^{9}. As observed for the H^{1} shifts, resonances due to the tertiary phosphine carbon atoms showed no abnormalities and occurred in the region normally appropriate for diamagnetic complexes.

TABLE 5

Hydrogen-1 and ^{13}C shifts (p.p.m.) of the complexes (I; R′ = Et) relative to the free hydrazides

Carbon or proton no.	^{1}H Direction of shift	^{1}H Range [a]	^{13}C Direction of shift	^{13}C Range [a]
1	Downfield	0.27		
2	Downfield	0.21—0.27	Downfield	19.0—9.2
3	Downfield	10.69—3.25	Upfield	26.1—13.8
4	Upfield	*b*	Downfield	84.2—88.3
5			Upfield	
6, 10	Upfield	5.4—2.7	Upfield	44.7—20.0
7, 9	Downfield	3.2—0.0	Downfield	91.3—42.0
8	Upfield	*ca.* 6 [c]	Downfield	75.0 [c]

[a] From R = 4-O_2N to 4-MeO. [b] Only for (I; R = R′ = H). [c] Only for R = H.

Conclusions.—The pattern of the large anomalous chemical shifts in the osmium diazene complexes is characteristic of paramagnetic species, but the complexes are apparently diamagnetic. However, unlike the spectra of paramagnetic complexes the large ^{1}H and ^{13}C shifts occur exclusively in one ligand, the ^{1}H, ^{13}C, and ^{31}P spectra of the tertiary phosphine ligands being normal. The direct temperature dependence suggests a second-order paramagnetic origin for the shifts since first-order paramagnetism results in an inverse temperature dependence.

The magnitude of the shifts is too great for their attribution to a ring-current effect, which usually causes shifts of *ca.* 1 p.p.m. at most. Moreover, the shifts are not an intrinsic property of the diazene ligand, as the ^{1}H n.m.r. spectrum of $PhCON_2Ph$ shows no abnormalities. Nor are they a general feature of chelated diazene complexes, because although the complexes (I) show resonances at 3.65 and 0.78 p.p.m. due to the *ortho* and *para* protons respectively of the C_6H_4R group, $[MoCl_2(NR')(R'{\cdot}N_2{\cdot}COR)(PMe_2Ph)]$ (R = R′ = aryl) has a completely normal ^{1}H n.m.r. spectrum.

We therefore suggest that the observed anomalous shifts may originate from mixing of a paramagnetic excited state, localised on the diazene ring, with an essentially diamagnetic ground state. The resulting unpaired electron density could then be too small to detect by bulk-susceptibility measurements or with certainty with e.s.r. However, evidence for a paramagnetic origin of the anomalous shifts is only circumstantial. Some INDO calculations on these complexes are to be carried out [9] and it is hoped that the results will provide further insight into the factors responsible for the observed spectra.

EXPERIMENTAL

All reactions were carried out under nitrogen. The substituted phenylhydrazines were prepared by established methods ($4\text{-}MeOC_6H_4NHNH_2$,[10] $4\text{-}MeC_6H_4NHNH_2$,[11] $4\text{-}ClC_6H_4NHNH_2$,[11] and $2,5\text{-}Cl_2C_6H_3NHNH_2$ [12]) or obtained commercially ($PhNHNH_2$, $4\text{-}NO_2C_6H_4NHNH_2$, and $4\text{-}MeC_6H_4NHNH_2{\cdot}HCl$). The *N*′-arylacylhydrazides, $RC_6H_4NHNHCOR'$, were prepared according to equations (1)

$$RC_6H_4NHNH_2 + (RCO)_2O \xrightarrow{Et_2O} RC_6H_4NHNHCOR' + R'CO_2H \quad (1)$$

$$RC_6H_4NHNH_2 + R'COCl \xrightarrow{C_5H_5N} RC_6H_4NHNHCOR' + C_5H_5N{\cdot}HCl \quad (2)$$

$$RC_6H_4NHNH_2 + R'CO_2Me \xrightarrow{\text{neat}} RC_6H_4NHNHCOR' + MeOH \quad (3)$$

(R = 4-MeO, R′ = Me and Et; R = 4-Me, R′ = Me and Et; R = 3-Me, R′ = Me; R = H, R′ = Me, Et, Pr^{n}, and $PhCH_2$; R = 4-Cl, R′ = Me and Et; R = 2,5-Cl_2, R′ = Me), (2) (R = H, R′ = Bu^{t}; R = 4-O_2N, R′ = Me or Et), and (3) (R = H or 4-Me, R′ = H) (elevated temperature).

I.r. spectra were recorded on Unicam SP 1 200 (Nujol mulls, 400—4 000 cm^{-1}) and Grubb–Parsons D.M.4 spectrometers (Nujol mulls, 200—500 cm^{-1}). Electronic spectra in dichloromethane solutions were obtained on a Unicam SP 800 spectrophotometer. The ^{1}H n.m.r. spectra were measured using JEOL PS-100 and Varian T-60 instruments generally in $CDCl_3$ solution with tetramethylsilane as

---

[9] G. A. Webb, personal communication.

[10] K. G. Blaikie and W. H. Perkin, jun., *J. Chem. Soc.*, 1924, **125**, 313.

[11] W. MacPherson and G. W. Stratton, *J. Amer. Chem. Soc.*, 1915, **37**, 906.

[12] I. M. Hunsberger, E. R. Shaw, J. Fugger, R. Ketcham, and D. Lednicer, *J. Org. Chem.*, 1956, **21**, 394.

internal standard. ^{13}C N.m.r. spectra were recorded on a JEOL PS-100 instrument operating in the Fourier-transform mode with $CDCl_3$ as internal standard. E.s.r. spectra were obtained on a Varian E3 spectrometer and magnetic moments were measured on Faraday balances. Molecular weights were determined osmometrically in benzene solutions on a Hitachi–Perkin-Elmer vapour-pressure osmometer 115, and m.p.s were recorded on a Köfler hot-stage in air and are uncorrected. Microanalyses for carbon, hydrogen, nitrogen, and chlorine were by Mr. and Mrs. A. G. Olney of Sussex University and those for chlorine and phosphorus by Dr. A. Bernhardt, Germany.

The complexes $[OsCl_3O(PPh_3)_2]$ and $[OsBr_3O(PPh_3)_2]$ were prepared by procedures described in the literature.[3]

Preparation of Dichlorobis(triphenylphosphine)osmium(II) *Complexes* with Chelated Diazene Ligands*, $[OsCl_2(RC_6H_4{\cdot}N_2{\cdot}COR')(PPh_3)_2]$, (I).—Since the method is general a typical preparation is described and analytical data, m.p.s, *etc.* are listed in Table 1.

(N-*Acetyl*-N′-*phenyldiazene*-ON)*dichlorobis*(*triphenylphosphine*)*osmium*(II), (I; R = H, R′ = Me). Trichloro-oxobis(triphenylphosphine)osmium(V) (0.50 g, 0.60 mmol), N′-phenylacetohydrazide (0.50 g, 3.33 mmol), and triphenylphosphine (1.9 g, 7.28 mmol) were heated under reflux in ethanol (50 cm^3) for 2 h under nitrogen. The system was filtered hot to give a brown microcrystalline solid, which was washed with ethanol and recrystallised from dichloromethane–ethanol as bright brown *needles* (0.19 g, 34%).

The dibromo-analogue $[OsBr_2(OCMe{\cdot}N_2{\cdot}Ph)(PPh_3)_2]$, (II), was obtained in the same way from tribromo-oxobis(triphenylphosphine)osmium(V) and recrystallised from benzene–ethanol. The other complexes, except (III—(VI) (Table 1), were obtained similarly.

Preparation of Dichlorobis(tertiary phosphine)osmium(II) *Complexes with Diazene Ligands*, $[OsCl_2(Ph{\cdot}N_2{\cdot}COR')(PR_3)_2]$ [(III)—(VI); R′ = Me *and* CH_2Ph].—These were prepared by tertiary phosphine exchange reactions starting from corresponding PPh_3 complexes. A typical procedure is described below.

(N-*Acetyl*-N′-*phenyldiazene*-ON)*dichlorobis*(*methyldiphenylphosphine*)*osmium*(II), (III; R = H, R′ = Me). Complex (I; R = H, R′ = Me) (0.46 g, 0.49 mmol) was dissolved in dry benzene (30 cm^3) and the solution was filtered. To the filtrate methyldiphenylphosphine (1.76 g, 8.80 mmol) was added and the mixture was heated under reflux for 1.5 h. The resulting brown solution was concentrated under reduced pressure to small volume and methanol (60 cm^3) was added. The solvent was evaporated under reduced pressure to *ca.* 20 cm^3, when the complex was precipitated as a brown microcrystalline *solid* which was filtered off and washed with precooled methanol (0.25 g, 51.5%).

The complexes (III; R = H, R′ = $PhCH_2$) and (IV)—(VI) were prepared similarly using the appropriate PPh_3 complexes and an excess of the tertiary phosphine.

Formation of Hydrido-complexes.—The complex $[OsCl_3O(PPh_3)_2]$ (0.50 g, 0.60 mmol), *N*′-2,5-dichlorophenylacetohydrazide (0.52 g, 2.37 mmol), and PPh_3 (2.44 g, 9.31 mmol) were heated under reflux for 3 h in ethanol. The resulting pale brown precipitate was filtered off, washed with ethanol, and recrystallised from dichloromethane (20 cm^3) and methanol (30 cm^3) as pale brown *crystals* (0.20 g, 30%), m.p. 160 °C (decomp.) (Found: C, 59.3; H, 4.5; Cl, 9.9; N, trace. $C_{54}H_{46}Cl_3OsP_3$ requires C, 59.8; H, 4.4; Cl, 9.8; N, 0%). I.r. spectrum in Nujol mull: ν(Os-H) 1 890m and 2 100 s cm^{-1}; ν(Os-Cl) 317, 290, and 270 cm^{-1}. In dichloromethane solution in air this complex reacted to give $[OsCl_3O(PPh_3)_2]$. The same hydride complex was also obtained from the analogous reactions of the oxo-osmium complex with *N*′-2,5-dichlorophenylpivalohydrazide or with (benzoylmethyl)phenyl amine.

We thank Dr. D. A. Lowe for recording the e.s.r. spectra, Dr. J. A. Connor for the *X*-p.e. spectra, and Drs. Ruth Lynden-Bell and G. A. Webb for helpful discussions.

[5/288 *Received, 12th February,* 1975]

---

* For the purposes of providing a name, the complexes have arbitrarily been written as derivatives of osmium(II). They could equally well have been defined as N′-arylacylhydrazido(2−)-*NO* complexes of osmium(IV) since there is no means of determining the metal oxidation state.