

Complexes of the Platinum Metals.

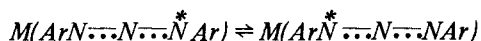
Part 22 [1]. Synthesis and Molecular Dynamics of 1,3-Diaryltriazenido Derivatives

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1,3-Diaryltriazenes, $ArN = N-NHAr$ ($Ar = Ph$, $p-MeC_6H_4$ and $p-MeOC_6H_4$) react with platinum metal halide complexes in the presence of triethylamine to afford products containing mono- or bidentate (chelate or bridging) 1,3-diaryltriazenido ligands. Complexes prepared in this manner include derivatives of ruthenium(II), $[Ru(ArN \cdots N \cdots NAr)_2(PPh_3)_2]$ and $[RuH(ArN \cdots N \cdots NAr)(CO)(PPh_3)_2]$; rhodium(I), $[Rh(ArN \cdots N \cdots NAr)(CO)_2]_2$, $[Rh(ArN \cdots N \cdots NAr)(C_6H_{12})(PPh_3)]$ and $[Rh(ArN \cdots N \cdots NAr)(CO)(PPh_3)_2]$; palladium(II) $[PdX(ArN \cdots N \cdots NAr)L_2]$ ($X = Cl$, $L = PPh_3$, PEt_3 , $AsPh_3$, $PMePh_2$; $X = Br$, $L = PMePh_2$; $X = I$, $L = PMe_2Ph$), and $[Pd(ArN \cdots N \cdots NAr)_2(PMe_2Ph)_2]$; and platinum(II), $[PtCl(ArN \cdots N \cdots NAr)L_2]$ ($L = PPh_3$, PEt_3 , and PEt_2Ph ; $L_2 = C_8H_{12}$). The intramolecular $N(1)-N(3)$ exchange process:



displayed by the monodentate 1,3-diaryltriazenido derivatives of rhodium(I), palladium(II) and platinum(II) have been studied by dynamic proton NMR spectroscopy, and thermodynamic parameters of activation have been determined. $\Delta H^\ddagger$ values were found to lie within the range ca. 32–44 kJ mol⁻¹ for the palladium(II) and platinum(II) complexes, $\Delta S^\ddagger$ values are all negative.

Introduction

The ability of 1,3-diaryltriazenido anions to function as monodentate or bidentate (chelate or bridging) ligands in transition metal complexes has been amply confirmed in recent years. Furthermore, the chemical and spectroscopic properties of these novel catenated nitrogen systems when bound to transition metals are the subject of continued interest

[2, 3]. In previous publications from our laboratory the synthesis of many new mono- and bi-dentate 1,3-diaryltriazenido complexes of the platinum group metals by the direct interaction of metal hydrides with 1,3-diaryltriazenes has been described [4, 5], and the dynamic intramolecular $N(1)-N(3)$ exchange of monodentate 1,3-diaryltriazenido ligands in platinum metal complexes has been noted [6]. We now describe a further range of platinum metal 1,3-diaryltriazenido derivatives synthesised by the treatment of platinum metal halide complexes with 1,3-diaryltriazenes in the presence of an organic base (triethylamine). The results of a more extensive dynamic NMR study on the kinetics of intramolecular $N(1)-N(3)$ exchange reactions occurring in monodentate 1,3-diaryltriazenido complexes of palladium(II) and platinum(II) are also discussed.

Experimental

Platinum metal salts were supplied by Johnson Matthey and Co. Ltd., and were converted into phosphine complexes by literature procedures. 1,3-Diaryltriazenes were prepared by treatment of diazonium salts with primary amines according to the method of Vogel [7]. Solvents were purchased from BDH and Co. Ltd., and were dried over molecular sieves. All reactions were performed under a nitrogen atmosphere but products were purified and handled in air before drying *in vacuo* at ca. 80–90 °C. Yields are based on platinum metal content. Micro-analyses, performed by the micro-analytical laboratory, University College London, and melting points, taken in sealed capillary tubes under nitrogen, are given in Table I. Infrared spectra were taken on a Perkin-Elmer 457 grating spectrometer using samples mullied in nujol. Routine proton NMR spectra were recorded on a Perkin-Elmer R12B 60 MHz spectrometer using samples dissolved in $CDCl_3$. Chemical shift data were referenced against internal TMS, and are quoted on the tau scale. Phosphorus NMR spectra were proton broad band decoupled, and were recorded at an

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TABLE I. Melting Point, Analytical and Proton NMR Data for 1,3-Diaryltriazenido Complexes.

Complex ^a	M.Pt. (°C)	Analysis Data ^b			$\tau(\text{Me})/\text{triazene}$	$\tau(\text{alkyl})/\text{PR}_3$
		%C	%H	%N		
Ru(dtt) ₂ PPh ₃ ₂	198–199	71.2 (71.55)	5.4 (5.45)	7.0 (7.8)	7.88	
Ru(dmt) ₂ (PPh ₃) ₂	168–170	67.05 (67.55)	5.05 (5.15)	7.95 (7.4)	6.63	
RuH(dpt)(CO)(PPh ₃) ₂	213–214	68.45 (69.15)	4.85 (4.85)	4.8 (4.95)		
RuH(dtt)(CO)(PPh ₃) ₂	217–218	70.15 (69.7)	5.25 (5.15)	4.75 (4.8)	7.85; 8.05	
RuH(dmt)(CO)(PPh ₃) ₂	205–207	66.8 (67.25)	5.15 (4.95)	4.6 (4.6)	6.61; 6.69	
[Rh(dpt)(CO) ₂] ₂		47.15 (47.35)	2.75 (2.85)	11.65 (11.85)		
[Rh(dmt)(CO) ₂] ₂		49.8 (50.1)	3.65 (3.70)	10.7 (10.95)	7.58	
Rh(dpt)(C ₈ H ₁₂)(PPh ₃)	134–136	67.6 (68.15)	5.65 (5.55)	6.35 (6.25)		
Rh(dtt)(C ₈ H ₁₂)(PPh ₃)	129–130	67.8 (68.85)	5.85 (5.9)	6.05 (6.0)	7.75	
Rh(dmt)(C ₈ H ₁₂)(PPh ₃)	121–122	64.75 (65.85)	5.75 (5.65)	5.05 (5.75)	6.60	
Rh(dpt)(CO)(PPh ₃) ₂	164–166	68.45 (69.1)	4.8 (4.85)	5.1 (4.95)		
Rh(dtt)(CO)(PPh ₃) ₂	161–163	69.0 (69.6)	5.0 (5.05)		7.85	
Rh(dmt)(CO)(PPh ₃) ₂	157–159	67.5 (67.2)	5.05 (4.85)	4.6 (4.6)	6.61	
PdCl(dpt)(PEt ₃) ₂	145–146	50.6 (50.2)	7.1 (7.0)	7.45 (7.3)		8.5(m); 8.8(m)
PdCl(dtt)(PEt ₃) ₂	139–140	51.75 (51.85)	7.4 (7.35)	7.15 (7.0)	7.71	8.5(m); 8.8(m)
PdCl(dpt)(PPh ₃) ₂ ½CH ₂ Cl ₂	239–241	65.55 (65.55)	4.65 (4.6)	4.9 (4.75)		
PdCl(dtt)(PPh ₃) ₂	226–229	67.45 (67.45)	4.95 (4.95)	4.4 (4.7)	7.75	
PdCl(dmt)(PPh ₃) ₂ ½CH ₂ Cl ₂	222–223	62.45 (62.85)	4.65 (4.7)	4.25 (4.35)	6.15	
PdCl(dtt)(AsPh ₃) ₂	228–230	61.65 (61.35)	4.5 (4.55)	3.95 (4.3)	7.70	
PdCl(dtt)(PMePh ₂) ₂ ½CH ₂ Cl ₂	199–201	61.3 (61.35)	5.1 (5.2)	5.3 (5.35)	7.70	8.3(t)
PdCl(dmt)(PMePh ₂) ₂	193–196	60.6 (60.3)	5.45 (5.05)	5.7 (5.25)	6.20	8.2(t)
PdBr(dtt)(PMePh ₂) ₂	185–187	59.1 (59.25)	4.85 (4.95)	5.1 (5.15)	7.95	8.2(t)
PdI(dtt)(PMe ₂ Ph) ₂	164–166	48.75 (49.1)	4.8 (4.95)	5.5 (5.7)	7.70	8.45(t)
Pd(dmt)(PMc ₂ Ph) ₂	170–171	47.55 (47.05)	4.85 (4.75)	5.65 (5.5)	6.20	8.35(t)
Pd(dtt) ₂ (PMe ₂ Ph) ₂	169–171	63.45 (63.6)	6.1 (6.05)	10.1 (10.1)	7.60	8.70(t)
Pd(dmt) ₂ (PMe ₂ Ph) ₂	175–177	58.4 (59.0)	5.55 (5.65)	9.3 (9.4)	5.95	8.65(t)
PtCl(dpt)(PEt ₃) ₂	231–233	43.2 (43.45)	6.05 (6.05)	6.35 (6.35)		8.4(m); 8.9(m)
PtCl(dtt)(PEt ₃) ₂	230–233	44.7 (45.2)	6.3 (6.4)	6.15 (6.1)	7.70	8.4(m); 8.9(m)
PtCl(dmt)(PEt ₃) ₂	216–220	42.3 (43.2)	6.05 (6.15)	5.8 (5.8)	6.20	8.4(m); 8.9(m)
PtCl(dpt)(PEt ₂ Ph) ₂	178–179	50.15 (50.65)	5.4 (5.3)	5.75 (5.55)		8.3(m); 9.1(m)
PtCl(dtt)(PEt ₂ Ph) ₂	188–189	51.5 (51.85)	5.7 (5.65)	5.35 (5.35)	7.70	8.3(m); 9.1(m)
PtCl(dmt)(PEt ₂ Ph) ₂	163–165	50.65 (49.85)	5.55 (5.4)	5.7 (5.15)	6.20	8.3(m); 9.1(m)
PtCl(dpt)(PPh ₃) ₂ ½CH ₂ Cl ₂	235–236	58.7 (58.65)	4.25 (4.15)	4.25 (4.25)		
PtCl(dtt)(PPh ₃) ₂	244–246	60.95 (61.3)	4.5 (4.55)	4.35 (4.3)	7.70	
PtCl(dmt)(PPh ₃) ₂ ½CH ₂ Cl ₂	228–230	58.1 (58.65)	4.25 (4.35)	3.55 (4.05)	6.20	
PtCl(dpt)(C ₈ H ₁₂)	171–174	45.35 (44.9)	4.20 (4.15)	7.9 (7.85)		
PtCl(dtt)(C ₈ H ₁₂)½CH ₂ Cl ₂	160–162	47.5 (45.75)	4.65 (4.6)	7.8 (7.2)	7.72	

^adpt = 1,3-diphenyltriazenide, dtt = 1,3-di-*p*-tolyltriazenide, dmt = 1,3-di-*p*-methoxyphenyltriazenide. ^bCalc. figures in parentheses.

operating frequency of 36.44 MHz using a Bruker HFX90 spectrometer operating in Fourier transform mode. Samples were dissolved in CDCl₃ and the spectra were referenced against external H₃PO₄ in the sense that resonances at low field are positive. Spectroscopic data are recorded in Table I. Details of instrumentation and experimental techniques used to collect the dynamic proton NMR data for

the kinetic study are given in the appropriate section below.

Bis(1,3-di-p-tolyltriazenido)bis(triphenylphosphine)-ruthenium(II)

1,3-Di-*p*-tolyltriazenide (0.2 g), dichlorotetrakis(triphenylphosphine)ruthenium (0.2 g) and triethylamine (1 ml) were heated together under reflux in

ethanol (10 ml) for 10 min. The precipitate, which deposited on cooling, was washed with water, methanol and light petroleum to yield the required product as red crystals (0.142 g, 81%). Bis(1,3-di-*p*-methoxyphenyltriazenido)bis(triphenylphosphine)ruthenium-(II) was similarly prepared as dark red crystals (87%).

Carbonylhydrido(1,3-di-p-tolyltriazenido)bis(triphenylphosphine)ruthenium(II)

Method a

Carbonyldichlorotris(triphenylphosphine)ruthenium (0.2 g) in benzene (10 ml), di-*p*-tolyltriazene (0.2 g) in ethanol (5 ml) and triethylamine (1 ml) were mixed and then heated under reflux for 40 min. The precipitate, which deposited on cooling, was filtered off and recrystallised from benzene-ethanol as orange crystals (0.128 g, 72%).

Method b

Carbonylbis(trifluoroacetato)bis(triphenylphosphine)ruthenium (0.2 g), 1,3-di-*p*-tolyltriazene (0.2 g) and triethylamine (1 ml) were heated together under reflux in ethanol for 30 min. The precipitate obtained from the cooled solution was filtered off and recrystallised from benzene-ethanol as orange crystals (0.16 g, 79%). The following were similarly prepared: carbonylhydrido(1,3-di-*p*-methoxyphenyltriazenido)-bis(triphenylphosphine)ruthenium(II) as red crystals (70%) and carbonylhydrido(1,3-diphenyltriazenido)-bis(triphenylphosphine)ruthenium as red crystals (65%).

Tetracarbonylbis-μ(1,3-di-p-tolyltriazenido)dirhodium(I)

Tetracarbonyl-μ-chlorodirhodium (0.1 g), triethylamine (1.0 ml) and 1,3-di-*p*-tolyltriazene (0.2 g) were heated together under reflux in ethanol (10 ml) for 15 min. The precipitate deposited was filtered off and recrystallised from hexane as red crystals (0.15 g, 77%). Tetracarbonylbis-μ-(1,3-diphenyltriazenido)dirhodium(I) was similarly prepared as dark red crystals (71%).

Cycloocta-1,5-diene(1,3-di-p-tolyltriazenido)(triphenylphosphine)rhodium(I)

Chloro(cycloocta-1,5-diene)triphenylphosphine-rhodium (0.2 g), 1,3-di-*p*-tolyltriazene (0.1 g) and triethylamine (1 ml) were shaken together in benzene (10 ml) for 30 min. Addition of methanol (10 ml) led to formation of an orange crystalline precipitate, which was recrystallised from benzene-methanol as orange crystals (0.237 g, 82%). Similarly prepared were: cycloocta-1,5-diene(1,3-diphenyltriazenido)-(triphenylphosphine)rhodium(I) as orange crystals (82%) and cycloocta-1,5-diene(1,3-di-*p*-methoxyphenyltriazenido)(triphenylphosphine)rhodium(I) as orange crystals (81%).

trans-Carbonyl(1,3-di-p-tolyltriazenido)bis(triphenylphosphine)rhodium(I)

Carbonylchlorobis(triphenylphosphine)rhodium (0.34 g), 1,3-di-*p*-tolyltriazene (0.12 g) and triethylamine (1 ml) were heated under reflux in 2-methoxyethanol (15 ml) for 1 h. The precipitate, which formed on diluting the solution with methanol (10 ml) and cooling, was recrystallised from dichloromethane-methanol as yellow crystals (0.25 g, 65%).

The following complexes were similarly prepared: *trans*-carbonyl(1,3-diphenyltriazenido)bis(triphenylphosphine)rhodium(I) as yellow crystals (70%) and *trans*-carbonyl(1,3-di-*p*-methoxyphenyltriazenido)bis(triphenylphosphine)rhodium(I) as brown crystals (70%).

trans-Chloro(1,3-di-p-tolyltriazenido)bis(triethylphosphine)palladium(II)

Dichlorobis(triethylphosphine)palladium (0.1 g), 1,3-di-*p*-tolyltriazene (0.06 g) and triethylamine (1 ml) in ethanol (10 ml) were heated under reflux for 15 min. The precipitate, which formed on cooling, was washed with ethanol and recrystallised from dichloromethane-ethanol to yield the required product as orange crystals (0.10 g 70%).

trans-Chloro(1,3-diphenyltriazenido)bis(triethylphosphine)palladium(II) was similarly prepared as orange crystals (76%).

The following complexes were similarly prepared from dichlorobis(triphenylphosphine)palladium: *trans*-chloro(1,3-di-*p*-tolyltriazenido)bis(triphenylphosphine)palladium(II) as red crystals (80%); *trans*-chloro(1,3-diphenyltriazenido)bis(triphenylphosphine)palladium(II) (4/1) dichloromethane solvate as red crystals (78%) and *trans*-chloro(1,3-di-*p*-methoxyphenyltriazenido)bis(triphenylphosphine)palladium-(II) (2/1) dichloromethane solvate as yellow crystals (80%).

Chloro(1,3-di-*p*-tolyltriazenido)bis(triphenylarsine)palladium(II) was similarly prepared as dark red crystals (75%) from dichlorobis(triphenylarsine)palladium.

The following were similarly prepared from dichlorobis(methyldiphenylphosphine)palladium: *trans*-chloro(1,3-di-*p*-tolyltriazenido)bis(methyldiphenylphosphine)palladium(II) (4/1) dichloromethane solvate as bright red crystals (68%) and *trans*-chloro(1,3-di-*p*-methoxyphenyltriazenido)bis(methyldiphenylphosphine)palladium(II) as yellow crystals (69%).

The following was similarly prepared from dibromobis(methyldiphenylphosphine)palladium: *trans*-bromo(1,3-di-*p*-tolyltriazenido)bis(methyldiphenylphosphine)palladium(II) as dark red crystals (66%).

The following were similarly prepared from diiodobis(dimethylphenylphosphine)palladium: *trans*-iodo(1,3-di-*p*-tolyltriazenido)bis(dimethylphenylphosphine)palladium(II) as orange-yellow crystals

(85%) and *trans*-iodo(1,3-di-*p*-methoxyphenyltriazenido)bis(dimethylphenylphosphine)palladium(II) as yellow–brown crystals (87%).

trans-Bis(1,3-di-*p*-tolyltriazenido)bis(dimethylphenylphosphine)palladium(II)

Dichlorobis(dimethylphenylphosphine)palladium (0.2 g), 1,3-di-*p*-tolyltriazeno (0.20 g) and triethylamine (1.0 ml) were heated together under reflux in ethanol (10 ml) for 15 min. The precipitate which formed on cooling was filtered off, recrystallised from dichloromethane/ethanol and dried *in vacuo* to yield the required product as yellow crystals (0.25 g, 69%). Similarly prepared was *trans*-bis(1,3-di-*p*-methoxyphenyltriazenido)bis(dimethylphenylphosphine)palladium(II) as orange crystals (69%).

cis-Chloro(1,3-di-*p*-tolyltriazenido)bis(triethylphosphine)platinum(II)

cis-Dichlorobis(triethylphosphine)platinum (0.2 g), 1,3-di-*p*-tolyltriazeno (0.1 g) and triethylamine (1.0 ml) were shaken together in benzene (15 ml) for 2 h. The solution was then filtered, diluted with methanol (10 ml) and left overnight. The resultant yellow precipitate was filtered off, washed with methanol (2 × 3 ml) and then crystallised from dichloromethane–methanol to yield yellow crystals (0.25 g, 91%).

The following were similarly prepared: *cis*-chloro(1,3-diphenyltriazenido)bis(triethylphosphine)platinum(II) as yellow crystals (88%), *cis*-chloro(1,3-di-*p*-methoxyphenyltriazenido)bis(triethylphosphine)platinum(II) as yellow crystals (90%).

cis-Chloro(1,3-di-*p*-tolyltriazenido)bis(diethylphenylphosphine)platinum(II)

Dichlorobis(diethylphenylphosphine)platinum (0.2 g), 1,3-di-*p*-tolyltriazeno (0.08 g) and triethylamine (1 ml) were stirred together in benzene (10 ml) until dissolved (2 h). The solution was then evaporated under reduced pressure to *ca.* 1 ml and diluted with methanol (3 ml) to induce precipitation of a yellow solid. The precipitate was filtered off, washed with methanol and recrystallised from dichloromethane–methanol to afford the required product as yellow crystals (0.234 g, 89%).

The following were similarly prepared: *cis*-chloro(1,3-diphenyltriazenido)bis(diethylphenylphosphine)platinum(II) as orange crystals (86%) and *cis*-chloro(1,3-di-*p*-methoxyphenyltriazenido)bis(diethylphenylphosphine)platinum(II) as yellow crystals (87%).

cis-Chloro(1,3-di-*p*-tolyltriazenido)bis(triphenylphosphine)platinum(II)

Dichlorobis(triphenylphosphine)platinum (0.2 g), 1,3-di-*p*-tolyltriazeno (0.06 g) and triethylamine (1 ml) were shaken in benzene (10 ml) until a clear

solution was obtained (2 h). Dilution with ethanol (10 ml) afforded a precipitate which was filtered off after several hours, washed with ethanol and recrystallised from dichloromethane–ethanol to yield the required product as yellow crystals (0.20 g, 81%).

The following were similarly prepared: *cis*-chloro(1,3-diphenyltriazenido)bis(triphenylphosphine)platinum(II) (2/1) dichloromethane solvate as orange crystals (80%) and *cis*-chloro(1,3-di-*p*-methoxyphenyltriazenido)bis(triphenylphosphine)platinum(II) (2/1) dichloromethane solvate as lime–yellow crystals (82%).

Chloro(cycloocta-1,5-diene)(1,3-di-*p*-tolyltriazenido)platinum(II) (4/1) dichloromethane solvate

Dichloro(cycloocta-1,5-diene)platinum (0.2 g), 1,3-diphenyltriazeno (0.12 g) and triethylamine (1 ml) were shaken together for several hours in benzene (10 ml). The filtered solution was diluted with methanol then allowed to stand for 12 h. The yellow precipitate was then filtered off, washed with ethanol and recrystallised from dichloromethane–methanol to afford the required compound as yellow crystals (0.14 g, 49%).

Chloro(cycloocta-1,5-diene) (1,3-diphenyltriazenido)platinum(II) was similarly prepared as yellow crystals (56%).

Kinetic Studies by Variable Temperature NMR Spectroscopy

The samples used in this study were prepared by the methods given in this paper and in a previous publication [5], isomeric purity was checked by spectroscopic methods. Spectra were obtained using a Bruker HFX-90 spectrometer equipped with a Nicolet 1080 data system for Fourier transform pulsed NMR. The variable temperature probe was fitted with a Bruker control, calibrated against a standard Varian methyl alcohol sample, to maintain selected temperatures to ± 0.5 K. The r.f. power was always maintained below the level at which saturation effects occurred. All spectra were obtained using samples dissolved in CD_2Cl_2 . Proton NMR chemical shifts are referenced to internal TMS and are reported on the tau scale. The calculations were performed by means of computer simulation using the Nicolet 1080 computer and a two-site exchange programme [8] based on the Gutowsky and Holm equations [9–11] for chemical exchange. This two-site exchange programme, for equal populations of the two sites, iteratively fits the chemical shifts, ν_1 and ν_2 , the linewidth parameter, $\Delta\nu_{1/2}$ (line-width at half height in absence of exchange), and the mean lifetime of the protons in each site, τ , to an NMR line shape broadened by chemical exchange.

The temperature dependence of the chemical shifts was taken into account by obtaining values for temperatures below coalescence directly from the

TABLE II. V.T. NMR and Kinetic Data for Palladium(II) and Platinum(II) Triazenido Complexes.

Complex	Ar	methyl resonances		coalescence temp. K	E_a kJ mol ⁻¹	$\Delta H^\ddagger$ kJ mol ⁻¹	$\Delta S^\ddagger$ JK ⁻¹ mol ⁻¹	$\Delta G^\ddagger$ a kJ mol ⁻¹
		ν_1 (τ)	ν_2 (τ)					
<i>trans</i> -[PdCl(ArN $\cdots$ N $\cdots$ NAr)(PPh ₃) ₂]	<i>p</i> -MeC ₆ H ₄	7.68	7.81	220 $\pm$ 1	38.2 $\pm$ 1.4	36.4 $\pm$ 1.4	-47 $\pm$ 6	46.5 $\pm$ 2.5
<i>trans</i> -[PdCl(ArN $\cdots$ N $\cdots$ NAr)(PPh ₃) ₂]	<i>p</i> -MeOC ₆ H ₄	6.19	6.30	221 $\pm$ 1	33.7 $\pm$ 1.4	31.9 $\pm$ 1.4	-66 $\pm$ 8	46.7 $\pm$ 2.6
<i>trans</i> -[PdBr(ArN $\cdots$ N $\cdots$ NAr)(PPh ₃) ₂]	<i>p</i> -MeC ₆ H ₄	7.67	7.79	204 $\pm$ 1	37.9 $\pm$ 1.6	36.1 $\pm$ 1.6	-34 $\pm$ 8	43.1 $\pm$ 2.6
[PdCl(ArN $\cdots$ N $\cdots$ NAr)(AsPh ₃) ₂]	<i>p</i> -MeC ₆ H ₄	7.71	7.83	222 $\pm$ 1	42.3 $\pm$ 1.0	40.5 $\pm$ 1.0	-27 $\pm$ 6	46.5 $\pm$ 2.2
<i>cis</i> -[PtCl(ArN $\cdots$ N $\cdots$ NAr)(PPh ₃) ₂]	<i>p</i> -MeC ₆ H ₄	7.61	7.71	215 $\pm$ 1	38.5 $\pm$ 1.0	36.7 $\pm$ 1.0	-41 $\pm$ 6	45.7 $\pm$ 2.2
<i>cis</i> -[PtCl(ArN $\cdots$ N $\cdots$ NAr)(PPh ₃) ₂]	<i>p</i> -MeOC ₆ H ₄	6.13	6.20	214 $\pm$ 1	45.4 $\pm$ 2.5	43.7 $\pm$ 2.5	-10 $\pm$ 13	46.2 $\pm$ 3.0

a These values calculated from rate constants at coalescence temperatures.

iteration of the programme. The chemical shift difference between the two sites was found to vary insignificantly over the temperature range studied. This difference was held constant for the calculations above the coalescence temperature.

In the region where the chemical exchange affects the bandshape, the parameters $\Delta\nu_{1/2}$ and τ are interdependent and cannot be separately determined. Where possible the line width was determined at high and low temperatures in the absence of exchange broadening and estimated for intermediate temperatures by interpolation from a plot of $\Delta\nu_{1/2}$ versus temperature. In the case of *trans*-[PdBr(ArN $\cdots$ N $\cdots$ NAr)(PPh₃)₂] (Ar = *p*-tolyl) where exchange broadening was still appreciable at the lowest temperatures permitted by the solvent, estimated values were used based on the values of similar compounds at the given temperature. In general the line width $\Delta\nu_{1/2}$ was observed to remain constant at a value of 2 Hz for temperatures above 220 K, and to increase to a value of 3.5–4.0 Hz at 190 K. This variation is probably due to viscosity broadening [12].

The mean lifetime, τ , was iteratively evaluated from exchange-broadened spectra at each of 8 to 12 different temperatures. Thermodynamic activation parameters were calculated according to Eyring theory [13]. The $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values were obtained from a least squares treatment of the corresponding rate data. The activation parameters are markedly affected by the line width, $\Delta\nu_{1/2}$, used. Therefore, the error in these values may be larger than that arrived at by the least squares analysis of the data. The small magnitudes of the chemical shift separations, $\nu_1 - \nu_2$, also acted as possible sources of further error by restricting the temperature range over which data could be collected. Estimated maximum errors of *ca.* 4 kJ mol⁻¹ in $\Delta H^\ddagger$ and *ca.* 12 JK⁻¹ mol⁻¹ in $\Delta S^\ddagger$ could arise from these factors. The effect of the uncertainty in $\Delta\nu_{1/2}$ is a minimum at the coalescence temperature because the broadening of the lines due to the exchange is a maximum. For this reason $\Delta G^\ddagger$ values are calculated from the rate data at the coalescence temperature. A maximum error of ± 3 kJ mol⁻¹ in $\Delta G^\ddagger$ is estimated. Thermodynamic parameters of activation are collected in Table II.

Results and Discussion

Synthesis and Characterisation of Complexes

The reactions of 1,3-diaryltriazenes with platinum metal hydrido or zero-valent complexes originally developed in our laboratory [4, 5], afford a clean, convenient route to many 1,3-diaryltriazenido derivatives. However, the range of accessible products is limited by the availability of suitable platinum metal precursors. Therefore, in an attempt to develop a more general synthesis based on metal halide com-

plexes but avoiding use of silver or alkali metal triazenides, we have investigated the reactions of halide complexes with 1,3-diaryltriazenes in the presence of an organic base (NEt_3). The results of this study, reported below, indicate that the new approach is successful in many instances. However, the reaction does not provide a reliable general synthesis since its outcome is too dependent upon the nature of the central metal atom and attached ancillary ligands. The products discussed below illustrate the range of syntheses successfully performed by this method.

The complexes $[\text{Ru}(\text{ArN}=\text{N}=\text{NAr})_2(\text{PPh}_3)_2]$ and $[\text{RuH}(\text{ArN}=\text{N}=\text{NAr})(\text{CO})(\text{PPh}_3)_2]$ were obtained as red or orange air-stable crystalline solids. They have previously been prepared by treatment of a variety of ruthenium precursors with 1,3-diaryltriazenes, and have both been shown by proton NMR to possess structures containing chelate triazenido ligands and *trans* pairs of triphenylphosphine ligands [5].

The complexes $[\{\text{Rh}(\text{ArN}=\text{N}=\text{NAr})(\text{CO})_2\}_2]$ were isolated as air-stable red crystals from the reactions of $[\{\text{RhCl}(\text{CO})_2\}_2]$ with 1,3-diaryltriazenes in the presence of triethylamine. Their infrared spectra show bonds characteristic of terminal carbonyl [$\nu(\text{CO}) = \text{ca. } 2000\text{--}2100\text{ cm}^{-1}$] and monodentate or bridging triazenide ligands [$\nu(\text{triazenide}) = \text{ca. } 1270\text{--}1330$ and 1210 cm^{-1}]. Related complexes $[\{\text{Rh}(\text{ArN}=\text{N}=\text{NAr})(\text{CO})_2\}_2]$ (Ar = Ph, *p*- $\text{C}_6\text{H}_4\text{F}$, *p*- $\text{C}_6\text{H}_4\text{Me}$) reported by Knoth [14] and Connelly [15] also show $\nu(\text{CO})$ bands at *ca.* 2000–2100 cm^{-1} and were formulated as 'folded' diaryltriazenido bridged binuclear species.

The complexes $[\text{Rh}(\text{ArN}=\text{N}=\text{NAr})(\text{C}_8\text{H}_{12})(\text{PPh}_3)]$ were obtained as air-stable orange crystals from the reaction of $[\text{RhCl}(\text{C}_8\text{H}_{12})(\text{PPh}_3)]$ with the appropriate triazene and triethylamine in cold benzene. The proton NMR spectrum confirms the proposed stoichiometry for each complex, and the infrared spectra indicate the presence of monodentate or possibly bridging triazenide ligands. However, the latter possibility is eliminated by molecular weight data which indicate that the complexes are mononuclear. The methyl groups in the 1,3-di-*p*-tolyltriazenido complex give rise to a single resonance. On the basis of this evidence we conclude that these compounds are square-planar rhodium(I) complexes containing monodentate triazenide ligands which are undergoing a rapid N(1)–N(3) exchange process.

The complexes *trans*- $[\text{Rh}(\text{ArN}=\text{N}=\text{NAr})(\text{CO})(\text{PPh}_3)_2]$ were obtained as air stable yellow or red crystals. Their infrared spectra display bands indicative of terminal carbonyl [$\nu(\text{CO}) = \text{ca. } 1955\text{ cm}^{-1}$] and monodentate (or bridging) triazenide ligands [$\nu(\text{triazenide})$ *ca.* 1280–1310 and 1210–1220 cm^{-1}]. Proton NMR spectra of the 1,3-di-*p*-tolyl

and 1,3-di-*p*-methoxyphenyl triazenido complexes each show a single resonance at temperatures down to 183 K. Phosphorus NMR spectra reveal the presence of a pair of equivalent ^{31}P nuclei in each complex [$\delta_{\text{PPh}_3} = \text{ca. } 35.5\text{ p.p.m.}$; $^1\text{J}(\text{RhP}) = \text{ca. } 135\text{ Hz}$]. These data are consistent with a four coordinate square planar *trans* structure in which the triazenide ligands are undergoing a very rapid intramolecular rearrangement. Complexes of this stoichiometry have previously been prepared [5, 14, 16, 17] and have been variously formulated as four-coordinate monodentate [5] or five-coordinate bidentate [14] triazenido complexes of rhodium(I).

The complexes *trans*- $[\text{PdX}(\text{ArN}=\text{N}=\text{NAr})(\text{PR}_3)_2]$ were obtained as dark red, air-stable crystals. The ^{31}P NMR spectra (proton decoupled; R = Ph) each consist of a singlet (δ_{PPh_3} *ca.* –23 to –24 p.p.m.) and are therefore indicative of *trans* stereochemistry. This assignment is supported in the case of the PMe_2Ph and PMePh_2 complexes by the NMR spectra of the methyl groups which generate virtual coupling 'triplet' patterns. The presence of monodentate triazenide ligands is indicated by the infrared spectra and by the dynamic proton NMR studies (see below) which establish that these ligands are undergoing rapid intramolecular N(1)–N(3) exchange at 298 K. Complexes of this stoichiometry have previously been prepared by the treatment of $[\text{PdCl}_2(\text{PPh}_3)_2]$ with lithium salts of 1,3-diaryltriazenes [18]. An X-ray diffraction study on $[\text{PdCl}(\text{ArN}=\text{N}=\text{NAr})(\text{PPh}_3)_2]$ (Ar = *p*-tolyl) has established the *trans* configuration and the presence of monodentate triazenide ligands [19].

The complex $[\text{PdX}(\text{ArN}=\text{N}=\text{NAr})(\text{AsPh}_3)_2]$ (Ar = *p*- $\text{C}_6\text{H}_4\text{Me}$) was obtained as a dark red solid. Owing to the absence of phosphorus nuclei it was not possible to make an unambiguous stereochemical assignment by NMR methods; however, by analogy with the corresponding triphenylphosphine complexes a *trans* configuration is preferred.

The complexes *trans*- $[\text{Pd}(\text{ArN}=\text{N}=\text{NAr})_2(\text{PMe}_2\text{Ph})_2]$ were obtained from *cis/trans*- $[\text{PdCl}_2(\text{PMe}_2\text{Ph})_2]$ as air-stable yellow or orange crystals. The same products were obtained from the corresponding dibromo complex using a larger excess of triazene; however, the diiodo complex gave *trans*- $[\text{PdI}(\text{ArN}=\text{N}=\text{NAr})(\text{PMe}_2\text{Ph})_2]$ as the only product even when a large excess of triazene was employed. These results are in accord with increasing Pd–X bond strength $\text{Cl} < \text{Br} < \text{I}$.

The absence of *cis* isomers amongst the palladium products even when *cis* dichloro complexes are used as precursors, presumably reflects the lability of these systems and the greater thermodynamic stability of the *trans* isomers.

The complexes *cis*- $[\text{PtCl}(\text{ArN}=\text{N}=\text{NAr})(\text{PR}_3)_2]$ were readily obtained by treatment of the corresponding dichloro complexes *cis*- $[\text{PtCl}_2(\text{PR}_3)_2]$

with the appropriate 1,3-diaryltriene and triethylamine in cold benzene. The relative reaction rates ($\text{Pt} > \text{Pd}$) observed in the palladium and platinum syntheses are contrary to the accepted labilities of these metals ($\text{Pd}^{\text{II}} \gg \text{Pt}^{\text{II}}$). However, the precursors *trans*- $[\text{PdCl}_2(\text{PR}_3)_2]$ and *cis*- $[\text{PtCl}_2(\text{PR}_3)_2]$ contain chloride ligands *trans* to chloride and phosphine respectively. Therefore the greater lability of the platinum complexes in these particular reactions can be attributed to the *trans* effect sequence $\text{PR}_3 \gg \text{Cl}$. Confirmation of this conclusion is provided by our observation that *trans*- $[\text{PtCl}_2(\text{PEt}_3)_2]$ failed to react with 1,3-diaryltriazenes in cold benzene over a period of two days. The infrared spectra of the complexes $[\text{PtCl}(\text{ArN} \cdots \text{N} \cdots \text{NAr})(\text{PR}_3)_2]$ show bands characteristic of monodentate 1,3-diaryltriazenido ligands. Proton decoupled ^{31}P NMR spectra demonstrate the presence of two non-equivalent phosphorus atoms and thus establish *cis*-stereochemistry [$\text{Ar} = p\text{-tolyl}$, $\text{R} = \text{Ph}$; $\delta_{\text{PPh}_3} -4.9$ p.p.m., $^1\text{J}(\text{PtP}) = 2920$ Hz and -2.5 p.p.m., $^1\text{J}(\text{PtP}) = 3800$ Hz]. Analogous compounds, previously prepared by treatment of $[\text{PtClH}(\text{PPh}_3)_2]$ [5] and $[\text{PtCl}_2(\text{PPh}_3)_2]$ [18] with 1,3-diaryltriazenes and lithium 1,3-diaryltriazenides respectively were shown to possess *cis*-stereochemistry by X-ray diffraction studies [20, 21]. A transcription error, involving transposition of ^{31}P NMR data for *cis* and *trans* isomers, led to the incorrect identification of some related platinum(II) diaryltriazenido complexes as *trans* isomers in a previous paper [5].

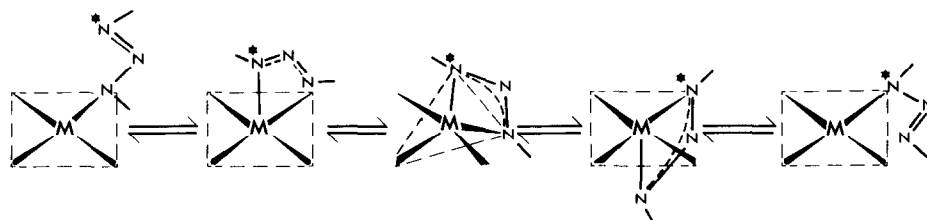
The complexes $\text{PtCl}(\text{ArN} \cdots \text{N} \cdots \text{NAr})(\text{C}_8\text{H}_{12})$ were obtained as air-stable yellow crystal by shaking together dichloro(cycloocta-1,5-diene)platinum, 1,3-diaryltriene and triethylamine in cold benzene. Their infrared spectra contain bands typical of monodentate triazenido ligands and at 298 K their ^1H NMR spectra ($\text{Ar} = p\text{-MeC}_6\text{H}_4$ or $p\text{-MeOC}_6\text{H}_4$) show a single methyl resonance, indicative of fluxional behaviour in solution.

Kinetic Studies on Monodentate 1,3-Diaryltriazenido Complexes

The dynamic N(1)–N(3) exchange behaviour of monodentate 1,3-diaryltriazenido ligands when bound to platinum group metals was first observed in our laboratory [6]. Preliminary studies indicated that the process proceeds by an intramolecular mechanism

involving a five coordinate chelate triazenido intermediate (Scheme 1), and that the activation energies are less than or equal to *ca.* 50 kJ mol $^{-1}$. In a brief report Toniolo *et al.* [18] subsequently confirmed these observations but did not report kinetic data for the processes involved. The present, more extensive, study was undertaken to confirm the proposed intramolecular mechanism and to investigate quantitatively the effect of changes in the nature of the central metal ion, *trans*-ligand and 1,3-diaryltriazenido substituent on the kinetics of the exchange process. Unfortunately the effects wrought by these changes have, for the most part, proved to be within the error limits of our data, and therefore do not provide a basis for quantitative discussion.

The data presented in Table II show that the values of $\Delta H^\ddagger$ span the range 32–44 kJ mol $^{-1}$ for all the palladium(II) and platinum(II) compounds studied. The corresponding ranges for E_a and $\Delta G^\ddagger$ are 34–45 kJ mol $^{-1}$ and 43–47 kJ mol $^{-1}$ respectively. Values of $\Delta S^\ddagger$ are negative in all cases, thereby indicating a more ordered transition state and thus supporting the involvement of a chelate triazenido intermediate. Addition of a small amount of pyridine leads to an increase in E_a and a change in $\Delta S^\ddagger$ from negative to positive. This observation indicates that the pyridine competes with the terminal (N3) nitrogen of the triazenido ligand for the axial coordination sites on the metal ion, and thus provides further evidence in favour of a chelate triazenido intermediate in the N(1)–N(3) interchange process. NMR spectra of mixed complexes provide evidence of relatively slow *intermolecular* triazenido ligand exchange. We therefore conclude that the fluxional process under investigation is *intramolecular* in nature and does not involve binuclear intermediates or the liberation of free triazenido anions. Confirmatory evidence for an *intramolecular* mechanism is provided by the concentration independence of the kinetic data. On the basis of earlier studies Toniolo *et al.* have already excluded mechanisms involving dissociation of an ancillary ligand (phosphine or halide) and concomitant formation of a four-coordinate chelate triazenido complex intermediate. The same authors considered, but rejected, mechanisms proceeding via σ, π -bonded triazenido intermediates. We therefore conclude that, on the basis of the evidence discussed above, the mechanism proposed



Scheme 1.

M = Pd, Pt

in our original work and represented in the scheme above is the most probable one for the processes under discussion.

The absence of significant differences in the rate data for palladium(II) and platinum(II) complexes is contrary to the established lability trend $\text{Pd}^{\text{II}} \gg \text{Pt}^{\text{II}}$, but can be explained in terms of the *trans* effect. The palladium and platinum complexes adopt *trans* and *cis* stereochemistry respectively, therefore the triazenide ligands in the former are *trans* to halide (or triazene) whereas those in the latter are *trans* to phosphine. Given the *trans* effect sequence $\text{PR}_3 \gg \text{halide} > \text{N-donors}$, it seems feasible that the greater *trans* effect of the phosphine ligand compensates for the lower lability of platinum relative to palladium. However, with this exception, the data do not permit any meaningful conclusions to be drawn concerning the influence, if any, of changes in *trans* ligand or triazenide substituent on the rate of the interchange process.

The ^1H NMR spectra of the rhodium(I) triazenido complexes are also consistent with the presence of monodentate triazenide ligands undergoing rapid N(1)–N(3) interchange. However, in common with many other rhodium(I) species, these complexes are very labile, and kinetic data could not be collected since their coalescence temperatures are below the range of our variable temperature probe (180 K).

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