Oxidative Substitution Reactions of Ruthenium(II) and Osmium(II) Complexes, $MCl_2(PPh_3)_3$ – New 1,3-Diaryltriazenido Derivatives $MCl_2(ArNNNAr)(PPh_3)_2$

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The ruthenium(II) complexes $RuX_2(PPh_3)_n$ (X = Cl, Br; n = 3, 4) and their osmium analogues have been extensively used as precursors in ligand substitution reactions leading to a wide variety of ruthenium(II) and osmium(II) species $MX_2L(PPh_3)_3$ or $MX_2L_2(PPh_3)_2$ [1]. They are also sensitive to aerobic oxidation in solution giving rise to triphenyl phosphine oxide and ill-characterized ruthenium(III) and osmium(III) products [1]. Some 10 years ago we demonstrated [2] that these two processes could be combined in a single stage oxidative substitution reaction (eqn. (1)) for the synthesis of new ruthenium(III) and osmium(III) carboxylates $MX_2(O_2CR)(PPh_3)_2$.

$$2MX_2(PPh_3)_3 + 2RCO_2H \xrightarrow{\text{air}} 2MX_2(O_2CR)(PPh_3)_2 + H_2O + 2Ph_3PO \quad (1)$$

In the present paper we describe the use of a similar oxidative substitution reaction to synthesize some related 1,3-diaryltriazenido derivatives $MCl_2(ArNNNAr)(PPh_3)_2$.

Experimental

The ruthenium complex $RuCl_2(PPh_3)_3$ was prepared by the improved procedure described below, $OsCl_2(PPh_3)_3$ [3] and the 1,3-diaryltriazenes [4] were synthesized by standard literature procedures. Light petroleum used throughout had a boiling point range 60–80 °C. Infrared spectra and magnetic susceptibilities were obtained using a Perkin-Elmer 983G infrared spectrometer and a Johnson Matthey magnetic susceptibility balance respectively. Analytical and spectroscopic data are given in Table I.

$RuCl_2(PPh_3)_3$

A solution of $RuCl_3 \cdot 3H_2O$ (0.2 g, 0.7 mmol) in ethanol (10 cm^3) was added to a stirred boiling solution of triphenylphosphine (1.2 g, 4.5 mmol) in ethanol (50 cm^3). After 30 min the mixture was

TABLE I. Melting Point, Analytical, Infrared Spectroscopic and Magnetic Data

Complex[a]	Melting point[b] (°C)	Analytical data[c] (%)			Infrared data[d] (cm^{-1})		Magnetic data
		C	H	N	ν(NNN)	ν(M–Cl)	μ_{eff} (BM)
$RuCl_2(PPh_3)_3$		67.40(67.65)	4.70(4.75)			315	
$RuCl_2(dptt)(PPh_3)_2$	216–218	64.50(65.10)	4.75(4.85)	4.45(4.55)	1497(s), 1243(s)	314(m), 280(m)	1.75
$RuCl_2(dpt)(PPh_3)_2$	210–212	64.05(64.55)	4.45(4.55)	4.75(4.70)	1480(s), 1247(s)	315(w), 295(m)	1.80
$RuCl_2(dpct)(PPh_3)_2$	244–246	60.40(59.95)	4.00(4.00)	4.20(4.35)	1481(s), 1265(s)	326(m), 303(w)	1.78
$OsCl_2(dptt)(PPh_3)_2$	266–270	59.90(59.45)	4.40(4.40)	4.10(4.15)	1500(m), 1263(s)	303(m), 295(sh)	1.82
$OsCl_2(dpt)(PPh_3)_2$	226–230	58.55(58.70)	4.00(4.10)	3.65(4.25)	1479(s), 1252(s)	305(m), 298(sh)	1.86
$OsCl_2(dpct)(PPh_3)_2$	285–288	55.00(54.85)	3.60(3.65)	3.85(4.00)	1481(s), 1262(s)	309(m), 305(sh)	1.83

[a] dptt, dpt and dcpt are di-*p*-tolyl-, di-phenyl- and di-*p*-chlorophenyl triazenide respectively [b] Melting points in sealed tubes under nitrogen. [c] Calculated figures in parentheses. [d] s = strong, m = medium, w = weak, *sh = shoulder.*

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cooled and the required product was filtered off as shiny red–brown crystals (0.6 g, 82%).

$RuCl_2(ArNNNAr)(PPh_3)_2$ ($Ar = p\text{-}MeC_6H_4$)

Dichlorotris(triphenylphosphine)ruthenium(II) (0.3 g, 0.31 mmol) was added to a solution of 1,3-di-*p*-tolyltriazene (0.14 g, 0.62 mmol) in benzene (10 cm^3) and the mixture was stirred at 70 °C for 1 h under aerobic conditions. After cooling to ambient temperature, the dark green solution was allowed to stand for 12 h during which time the product precipitated. Crystallization from dichloromethane/ethanol, followed by washing with ethanol and light petroleum afforded green microcrystals (0.20 g, 70%).

$RuCl_2(ArNNNAr)(PPh_3)_2$ ($Ar = C_6H_5$) was similarly prepared as green microcrystals (61.5%).

$RuCl_2(ArNNNAr)(PPh_3)_2$ ($Ar = p\text{-}ClC_6H_4$) was similarly prepared as green microcrystals (74%).

$OsCl_2(ArNNNAr)(PPh_3)_2$ ($Ar = p\text{-}MeC_6H_4$)

Dichlorotris(triphenylphosphine)osmium (0.2 g, 0.19 mmol) was added to a solution of 1,3-di-*p*-tolyltriazene (0.14 g, 0.62 mmol) in benzene (10 cm^3) and the mixture stirred at 70 °C for 1 h under aerobic conditions. After cooling to ambient temperature, the dark green solution was diluted with light petroleum (10 cm^3) and allowed to stand for 12 h. The solid which deposited was crystallized from dichloromethane/ethanol, washed successively with ethanol and light petroleum, then dried *in vacuo* to yield the required product as green microcrystals (0.05 g, 26%).

$OsCl_2(ArNNNAr)(PPh_3)_2$ ($Ar = C_6H_5$) was similarly prepared as green microcrystals (37%).

$OsCl_2(ArNNNAr)(PPh_3)_2$ ($Ar = p\text{-}ClC_6H_4$) was similarly prepared as green microcrystals (35%).

Results and Discussion

Benzene solutions of ruthenium(II) and osmium(II) complexes $MCl_2(PPh_3)_3$ undergo rapid aerobic oxidation at *ca.* 70 °C in the presence of 1,3-diaryltriazenes to afford the corresponding 1,3-diaryltriazenido complexes $MCl_2(ArNNNAr)(PPh_3)_2$ ($Ar = p\text{-}C_6H_4X$; X = H, Me or Cl) as green, air-stable microcrystals. The osmium complexes are identical with, or analogous to, the products $OsX_2(PhNNNPh)(PPh_3)_2$ (X = Cl or Br) previously obtained by Armstrong and Walton [5] from the reactions of Li[PhNNNPh] with $OsX_4(PPh_3)_2$ or $OsX_2(O)_2(PPh_3)_2$. In particular magnetic moment measurements on our products confirm the presence of low spin d^5 ruthenium(III) and osmium(III) ions thus supporting the ESR data reported by the previous authors [5]. The paramagnetic character of ruthenium(III) and osmium(III) species precludes the use of high resolution NMR spectroscopy in structural investigations and consequently forces reliance on vibrational spectroscopy and X-ray diffraction methods as the main techniques for arriving at stereochemical assignments. In our carlier work [2] on the carboxylate complexes $MX_2(O_2CR)(PPh_3)_2$ we tentatively assigned *trans* halide stereochemistry on the basis of a strong sharp single absorption at *ca.* 365–335 cm^{-1} in the infrared spectra of the ruthenium chloro derivatives $RuCl_2(O_2CR)(PPh_3)_2$ which was absent from the spectra of the corresponding bromides. However, a recent X-ray diffraction study [6] on the related osmium complex $OsBr_2(O_2CMe)(PPh_3)_2$ has established that for this complex at least the stereochemically preferred *cis*-halide/*trans*-phosphine structure is adopted. The presence of bands assigned to ν(M–Cl) at *ca.* 320 and 295 cm^{-1} (M = Ru) or *ca.* 305 and 300 cm^{-1} (M = Os) in the infrared spectra of the triazenide complexes $MCl_2(ArNNNAr)(PPh_3)_2$ currently under discussion strongly suggests that these species also adopt the *cis*-halide/*trans*-phosphine stereochemistry.

Work in our laboratory has shown that oxidative substitution reactions provide a route to ruthenium(III) and osmium(III) products of the general form $MCl_2(chelate)(PPh_3)_2$ in which the chelating ligands are the conjugate bases of carboxylic acids [2] β-diketones [7] and certain Schiff bases [8]. Further studies on these and some related systems are in progress in an attempt to determine the generality of the oxidative substitution process.

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