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$$\label{eq:relation} \begin{split} & \text{Triazenide complexes of iridium. Evidence for $[Ir(\eta^1-N_3Ph_2)(HN_3Ph_2)(1,5-cod)]$, structures of $[Ir_2(\mu-OMe)_2(1,5-cod)_2]$, $[Ir_2(\mu-N_3Ph_2)_2(1,5-cod)_2]$, $[Ir(\eta^2-N_3Ph_2)(H)(SiPh_3)(1,5-cod)]$, $[Ir(\eta^2-N_3Ph_2)(H)(SnPh_3)(1,5-cod)]$ and $[Ir(\eta^2-N_3Ph_2)(SC_6F_5)_2(1,5-cod)]$} \end{split}$$

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Triazenide complexes of iridium. Evidence for $[Ir(\eta^1-N_3Ph_2)(HN_3Ph_2)(1,5-cod)]$, structures of $[Ir_2(\mu-OMe)_2(1,5-cod)_2]$, $[Ir_2(\mu-N_3Ph_2)_2(1,5-cod)_2]$, $[Ir(\eta^2-N_3Ph_2)(H)(SiPh_3)(1,5-cod)]$, $[Ir(\eta^2-N_3Ph_2)(H)(SnPh_3)(1,5-cod)]$ and $[Ir(\eta^2-N_3Ph_2)(SC_6F_5)_2(1,5-cod)]$.

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ABSTRACT

The reaction of $[Ir_2(\mu-OMe)_2(1,5-cod)_2]$ with diphenyltriazene gives a product, formulated as $[Ir(\eta^{1}-N_3Ph_2)(HN_3Ph_2)(1,5-cod)]$ on the basis of NMR data, which dimerises slowly in solution forming $[Ir_2(\mu-N_3Ph_2)_2(1,5-cod)_2]$ and which reacts with SiHPh3, SnHPh3 and C₆F₅SH to give $[Ir(\eta^{2}-N_3Ph_2)(H)(SiPh_3)(1,5-cod)]$, $[Ir(\eta^{2}-N_3Ph_2)(H)(SnPh_3)(1,5-cod)]$ and $[Ir(\eta^{2}-N_3Ph_2)(SC_6F_5)_2(1,5-cod)]$ respectively.

1. Introduction

The triazenide ion, most notably in the diaryl form, has recently attracted attention as a ligand of potential interest in homogenous catalysis because of its versatility in modes of binding to a metal and the relative ease with which the steric and electronic properties can be adjusted by choice of appropriate substituents for the aryl groups. Diphenyltriazenide and derivatives in which the phenyl groups carry substituents have been used in studies of the chemistry of d block [1-73], main group [54, 74-81] and f block [57, 78, 82, 83] metals where the triazenide ligand exhibits the bonding modes η^1 [1-8, 57], η^2 (nonbridging) [1, 6, 9-33, 54-58, 73-83] and bridging [21, 28, 34-54, 60-72]. Other, less common, bonding modes include chelation of one metal atom while bridging to a second metal atom *via* one of the nitrogens (which binds to both metal atoms) [43] and the use of two adjacent nitrogens to bind to a metal atom while the third nitrogen binds to a second metal atom [66, 67, 76]. Many triazenide complexes are now being prepared in which substituents on the N₃Ph₂ phenyl groups are also involved in bonding to a metal atom [55-73] leading, in some cases, to

polynuclear complexes [62, 64, 66, 67] and macrocycles [65]. With $PhN_3(C_6H_4-2-X)$ where the substituent X is N_3Ph , each triazenide group binds through a single nitrogen to give a dianionic chelating ligand [59].

Some triazenide complexes have been shown to possess high catalytic activity. For example $[M(n^2 - N_3Ar_2)(N(SiMe_3)_2)(THF)_n]$ (M = Ca, n = 2; m = Sr, n = 3; Ar = 2,6-diisopropylphenyl) is catalytically active in the intramolecular hydroamination of 1-amino-2,2-diphenylpent-4-ene to form 2-methyl-4,4-diphenylpyrrolidine [76], $[Ru(n^2 - N_3(p-Tol)_2)(n^6 - p-cymene)(Bu^t NC)]^+$ (and related Ru and Os complexes) is a good catalyst for the hydrogenation of 2-cyclohexen-1-one and cinnamaldehyde [31] and $[M\{\{2-(2,4,6-Pr^i_3C_6H_2)C_6H_4\}_2N_3\}(AIMe_4)_2]$ (M = Y, La, Nd, Lu), in which the triazenide phenyl groups carry very bulky substituents, have found use as precatalysts which, together with cocatalysts $[Ph_3C][B(C_6F_5)_4]$ and $[PhNMe_2H][B(C_6F_5)_4]$ are active in the polymerisation of isoprene [83]. Electrochemical studies of complexes in which the substituent X on the triazenide aryl group $(N_3(C_6H_4-4-X)_2)$ is varied indicate a correlation between the electronic properties of X, as quantified by the Hammett parameter σ , and the oxidation potential(s) of the complexes for $[Rh_2(CO)_4(\mu-N_3(C_6H_4-4-X)_2)]$ (X = H, Me, Et, OMe, CN, F, Cl, Br) [48] and $[Ru(n^2-N_3(C_6H_4-4-X)_2)(H)(CO)(PPh_3)_2]$ (X = H, Me, OMe, Cl, NO₂) [32]. The latter complex (ligand $N_3(C_6H_4-4-CH_3)_2)$ is an effective catalyst for the transfer hydrogenation of aldehydes and ketones [32].

A number of iridium triazenide complexes have been reported. These have Ir(III) with a η^2 (nonbridging) N₃Ar₂ [9, 10, 19, 20], Ir(I) with a bridging N₃Ar₂ (Ar = Ph, Tol) [3, 34-36, 49], Ir(II) with bridging N₃Tol₂ [28], and Ir(I) with an η^1 -bound triazenide [1, 4], of which three have been structurally characterised [4, 28, 49]. In the present study we describe some chemistry of an unstable triazenide complex of Iridium(I).

2. Experimental

2.1 Materials

Dichloromethane was distilled from P_2O_5 . 1,5-cyclooctadiene, diethyl ether, benzene and n-hexane were dried over calcium hydride; other materials were of the highest available purity and were used without further treatment. All operations were performed under an argon atmosphere.

2.1.1 Synthesis of $[Ir_2(\mu-OMe)_2(1,5-cod)_2]$ (1)

The complex was prepared using the method of Robinson and Shaw [84] by which chloroiridic acid is converted firstly into $[Ir_2(\mu-Cl)_2(H)_2Cl_2(1,5-cod)_2]$, with 1,5 cyclooctadiene in boiling ethanol, and this intermediate product, when treated with sodium carbonate in hot methanol, gives **1**. The crude product obtained from a reaction using 2.825 g of H₂IrCl₆ was recrystallized from dichloromethane/methanol to give **1** as yellow crystals (0.275 g), yield over two steps 12% (Robinson and Shaw report a yield of 13%). ¹H NMR (CDCl₃, 300 K) δ 3.55 (mult, 4H, alkene), 3.25 (s, 3H, OMe), 2.23 (mult, 4H, CH₂), 1.37 (mult, 4H, CH₂); ¹³C NMR (CDCl₃, 300 K) δ 56.36 (alkene), 54.24 (OMe), 31.41 (CH₂). Anal. calc. for C₁₈H₃₀Ir₂O₂: C, 32.62; H, 4.56. Found: C, 32.48; H, 4.54.

2.1.2 In situ preparation of $[Ir(N_3Ph_2)(HN_3Ph_2)(1,5-cod)]$ (2a)

A solution of $[Ir_2(OMe)_2(1,5-cod)_2]$ (0.007 g, 0.021 mmol) in toluene-d8 (0.6 ml) at room temperature was treated with diphenyltriazene (0.0084 g, 0.042 mmol), shaken quickly to dissolve the solid and the dark red solution transferred to an NMR tube and immediately cooled to < -70 °C. ¹H NMR (toluene-d8, 198 K) δ 14.07 (s (br), 1H, NH), 7.93 (s (br), 4H, Ph *ortho*), 7.53 (s (br), 4H, Ph *ortho*), 7.12 (mult (br), 8H, Ph *meta*), 6.89 (mult (br), 4H, Ph *para*), 3.74 (s (br), 4H, alkene), 2.30 (s (br), 4H, CH₂), 1.45 (s (br), 4H, CH₂); ¹³C NMR (toluene-d8, 198 K) δ 149.34 (Ph *ipso*), 144.46 (Ph' *ipso*), 129.0 (obscured by toluene signal, Ph *meta*), 124.5 (obscured by toluene signal, Ph *meta*), 124.5 (obscured by toluene signal, Ph *para*), 32.77 (br, CH₂).

2.1.3 Synthesis of $[Ir_2(\mu - N_3Ph_2)_2(1, 5 - cod)_2]$ (3)

Solutions of $[Ir_2(OMe)_2(1,5-cod)_2]$ (0.020 g, 0.060 mmol based on Ir) in diethyl ether (1 ml) and diphenyltriazene (0.012 g, 0.061 mmol) in diethyl ether (1 ml) were mixed at room temperature with an immediate colour change to dark red. The solution was allowed to stand at room temperature for 24 h. The product was obtained as black crystals, yield 0.019 g (63%). ¹H NMR (CDCl₃, 215 K) δ 7.86 (d (J 7.9), 4H, Ph), 7.45 (s, 2H, Ph), 7.42 (mult, 2H, Ph), 7.32 (mult, 4H, Ph), 7.27 (mult, 2H, Ph), 7.23 (mult, 4H, Ph), 7.16 (mult, 1H, Ph), 6.72 (mult, 1H, Ph), 4.35 (mult, 2H, alkene), 3.98 (mult, 2H, alkene), 3.87 (mult, 2H, alkene), 3.64 (mult, 2H, alkene), 2.72 (mult, 4H CH₂), 2.40 (mult, 4H, CH₂), 1.78 (mult, 4H, CH₂), 1.71 (mult, 4H, CH₂); ¹³C NMR (CDCl₃, 215 K) δ 151.66 (Ph), 149.09 (Ph), 128.43

(Ph), 128.24 (Ph), 128.02 (Ph), 127.74 (Ph), 125.68 (Ph), 125.21 (Ph), 124.89 (Ph), 124.03 (Ph), 123.71 (Ph), 75.36 (alkene), 71.53 (alkene), 63.27 (alkene), 56.73 (alkene), 32.26 (CH₂), 32.07 (CH₂), 30.94 (CH₂), 30.34 (CH₂); ¹⁵N NMR (CDCl₃, 223 K), δ -132.6 (N1, N3). Anal. calc. for C₄₀H₄₄IrN₆: C, 48.37; H, 4.47; N, 8.46. Found: C, 48.74; H, 4.19; N, 8.45.

2.1.4 Synthesis of $[Ir(\eta^2 - N_3Ph_2)(H)(SiPh_3)(1,5-cod)]$ (4)

Solutions of [Ir₂(OMe)₂(1,5-cod)₂] (0.020 g, 0.060 mmol based on Ir) in diethyl ether (1 ml) and diphenyltriazene (0.0012 g, 0.061 mmol) in diethyl ether (1ml) were mixed at room temperature, accompanied by an immediate colour change to dark red and, within 1 min, treated with a solution of triphenylsilane (0.050 g, 0.19 mmol) in diethyl ether (0.5 ml). Within a few seconds the colour of the solution lightened slightly. After 5 min the solution was concentrated, treated with hexane and allowed to stand at -20 °C for two days to give the product as red crystals. Yield 0.034 g (75 %). 1H NMR (C₆D₆, 300 K) δ 7.74 (mult, 6H, PhSn ortho), 7.38 (mult, 2H, PhN H10, H14), 7.36 (mult, 2H, PhN, H16, H20), 7.29 (mult, 2H, PhN H17, H19), 7.12 (mults, 9H, PhSn meta, para), 7.08 (mult, 1H, PhN H18), 7.03 (mult, 2H, PhN H11, H13), 6.79 (mult, 1H, PhN H12), 5.33 (mult, 1H, alkene H6), 4.16 (mult, 1H, alkene H5), 3.96 (mult, 1H, alkene H1), 3.81 (mult, 1H, alkene H2), 2.78 (mult, 1H, CH₂ H8a), 2.47 (mult, 1H, CH₂ H8b), 2.31 (mult, 1H, CH₂ H4b), 2.03 (mult, 1H, CH₂ H4a), 1.96 (mult, 1H, CH₂ H3b), 1.64 (mult, 1H, CH₂ H7b), 1.23 (mult, 1H, CH₂ H3a), 1.12 (mult, 1H, CH₂ H7a), -15.30 (s, 1H, IrH); ¹³C NMR (C₆D₆, 300 K), δ 149.09 (C15), 145.70 (C9), 140.79 (PhSi C *ipso*), 136.93 (PhSi C *ortho*), 128.94 (C17, C19), 128.82 (C11, C13), 128.08 (obscured by benzene signal), PhSi C para), 127.29 (PhSi C meta), 124.66 (C18), 124.43 (C12), 117.92 (C16, C20) 115.98 (C10, C14), 106.01 (C5), 99.08 (C6), 67.83 (C2), 65.25 (C1), 40.53 (C8), 30.47 (C3), 28.78 (C4), 27.25 (C7); ¹⁵N NMR (C₆D₆, 300 K), δ -167.7 (N1), -162.1 (N3); ²⁹Si NMR (C₆D₆, 300 K) δ -7.61. Anal. calc. for C₃₈H₃₈IrN₃Si: C, 60.29; H, 4.93; N, 5.55. Found: C, 60.66; H, 5.19; N, 5.47.

2.1.5 Synthesis of $[Ir(\eta^2 - N_3Ph_2)(H)(SnPh_3)(1,5-cod)]$ (5)

Solutions of $[Ir_2(\mu-OMe)_2(1,5-cod)_2]$ (0.020 g, 0.060 mmol based on Ir) in diethyl ether (1ml) and diphenyltriazene (0.012 g, 0.061 mmol) in diethyl ether (1ml) were mixed at room temperature. An immediate colour change to dark red was observed. Within 1 min triphenyltin hydride (0.030 g, 0.086 mmol) was added, accompanied by a slight lightening in colour. The mixture was concentrated, treated with hexane and allowed to stand at -20 °C for 20 h to give the product as dark red crystals. Yield 0.032 g (63%). ¹H NMR (C₆D₆, 300 K) δ 7.71 (mult, 6H, PhSn *ortho*), 7.42 (dd (J

8.6, 1.1), 2H, PhN H10, H14), 7.36 (dd (J 8.6, 1.1), 2H, PhN H16, H20), 7.21 (dd (J 8.4, 7.4), 2H, PhN H17, H19), 7.15, 7.13 (obscured by benzene signal, mults, PhSn *meta*, *para* respectively), 7.03 (mult, 2H, PhN H11, H13), 7.03 (mult, 1H, PhN H18), 6.79 (tt (J 7.3, 1.0), 1H, PhN H12), 5.05 (mult, 1H, alkene H6), 4.30 (mult, 1H, alkene H1), 4.25 (mult, 1H, alkene H2), 3.89 (mult, 1H, alkene H5), 2.36 (mult, 1H, CH₂ H8a), 2.17 (mult, 1H, CH₂ H8b), 2.11 (mult, 1H, CH₂ H4b), 1.90 (mult, 1H, CH₂ H3b), 1.75 (mult, 1H, CH₂ H4a), 1.70 (mult, 1H, CH₂ H7b), 1.20 (mult, 1H, CH₂ H3a), 1.09 (mult, 1H, CH₂ H3b), 1.75 (mult, 1H, CH₂ H4a), 1.70 (mult, 1H, CH₂ H7b), 1.20 (mult, 1H, CH₂ H3a), 1.09 (mult, 1H, CH₂ H7a), -15.11 (s with Sn satellites (J(^{119/117}Sn, ¹H) 30.0, 1H, IrH)); ¹³C NMR (C₆D₆, 300 K), δ 149.58 (C15), 146.12 (C9), 142.98 (PhSn C *ipso*), 137.77 (s with Sn satellites (J(^{119/117}Sn, ¹³C) 35) PhSn C *ortho*), 129.08 (C17, C19), 128.93 (C11, C13), 128.20 (PhSn C *meta*), 127.94 (PhSn C *para*), 124.91 (C18), 124.70 (C12), 118.20 (C16, C20), 115.93 (C10, C14), 97.89 (C5), 89.25 (C6), 67.26 (C2), 64.65 (C1), 39.21 (C8), 31.41 (C3), 29.12 (C7), 28.62 (C4); ¹⁵N NMR (C₆D₆, 300 K) δ -174.6 (N1), -165.9 (N3); ¹¹⁹Sn NMR (C₆D₆, 300 K) δ -175.17. Anal. calc for C₃₈H₃₈IrN₃Sn: C, 53.84; H, 4.40; N, 4.96. Found: C, 53.63; H, 4.22; N, 5.03.

2.1.6 Synthesis of $[Ir(\eta^2 - N_3Ph_2)(SC_6F_5)_2(1, 5 - cod)](C_6H_6)$ (6)

Solutions of $[Ir_2(\mu-OMe)_2(1,5-cod)_2]$ (0.023 g, 0.069 mmol based on Ir) in benzene (1ml) and diphenyltriazene (0.015 g, 0.076 mmol) in benzene (1ml) were mixed at room temperature, accompanied by an immediate colour change to dark red. Within 1 min the mixture was treated with pentafluorophenyl thiol (0.020 g, 0.10 mmol) to give, after a few seconds an orange coloured solution. Hexane was added and the solution allowed to stand at -20 °C for 12 days, during which time red crystals and a yellow powder formed. The product was obtained as red needles, yield 0.013 g (20%). ¹H NMR (C₆D₆, 300 K) δ 6.96 (mult, 4H, Ph H *meta*), 6.82 (mult, 2H, Ph H *para*), 6.49 (mult, 4H, Ph H *ortho*), 5.40 (mult, 4H, alkene), 2.70 (mult, 4H, CH₂), 1.09 (mult, 4H, CH₂); ¹³C NMR (C₆D₆, 300 K), δ 142.66 (Ph C *ipso*), 128.81 (Ph C *meta*), 126.02 (Ph C *para*), 115.34 (Ph C *ortho*), 88.41 (alkene), 29.13 (CH₂); ¹⁵N NMR (C₆D₆, 300 K) δ -153.0. Anal. calc for C₃₈H₂₈F₁₀IrN₃S₂: C, 46.90; H, 2.90; N, 4.32. Found: C, 46.79; H, 2.69; N, 4.42. The yellow product (0.003 g) was identified as [Ir₂(μ -SC₆F₅)₂(1,5-cod)₂] [85].

2.2 NMR Spectroscopy

Spectra were recorded on Bruker DRX 400 and Avance 400 spectrometers operating at 400.13 MHz (¹H), 100.61 MHz (¹³C), 40.35 MHz (¹⁵N), 79.49 MHz (²⁹Si) and 149.19 MHz (¹¹⁹Sn) and calibrated relative to TMS (¹H (int. standard), ²⁹Si (ext. standard)), CDCl₃ at 77.00 ppm, C_6D_6 at 128.03 ppm and

toluene-d8 at 2.085 ppm (13 C), CH₃NO₂ (ext. standard; 15 N) and SnMe₄ (ext. standard; 119 Sn). Signals in the 1 H and 13 C spectra were assigned using COSY, NOESY, HSQC and HMBC; the 15 N spectra were obtained using 15 N- 1 H HMBC.

The full assignment of the NMR signals for 5 is summarised as follows. The labelling scheme for atoms is that used in the crystallographic structural diagram. The NOESY spectrum of 5 shows a through space interaction between the hydride attached to iridium and hydrogens with chemical shifts 7.71 (PhSn ortho), 7.42 (PhN H10, H14), 5.05 (alkene H6), 4.30 (alkene H1), 2.17 (H8b) and 1.70 (H7b). COSY shows hydrogens with δ 7.42, 7.03 and 6.79 to belong to one PhN (positions 10-14) and hydrogens with δ 7.36, 7.21 and 7.03 to belong to the second PhN (positions 16-20). The identification of these signals as arising from the triazenide phenyl groups is confirmed by the ¹⁵N-¹H HMBC spectrum which shows ¹⁵N signals aligned with ¹H signals at δ 7.42 (H10, H14) and 7.36 (H16, H20). A NOESY interaction between hydrogens at δ 7.36 and the hydrogen at δ 4.25 allows alkene H5 to be identified, and an interaction between hydrogens at δ 7.71 (SnPh) and the hydrogens at δ 4.30 allows alkene H1 to be identified thus establishing which signals arise from the axial alkene (H5, H6) and from the equatorial alkene (H1, H2). The HSQC spectrum shows pairs of signals at δ 2.36 and 2.17, 2.11 and 1.75, 1.90 and 1.20, 1.70 and 1.09 each to belong to hydrogens of a CH_2 group; from the COSY spectrum these can be identified as CH₂ groups 8, 4, 3 and 7 respectively by coupling to alkene hydrogens. The relative orientations of the hydrogens in each CH₂ group (subscript 'a' indicating a C-H bond pointing up with respect to the iridium atom; 'b' pointing down) are given by the NOESY interactions between the hydride ligand and H δ 2.17, H δ 1.70 (8b and 7b respectively) and between hydrogens δ 7.37 and H δ 2.11, H δ 1.90 (4b and 3b respectively). Carbon signals were assigned using HSQC and HMBC spectra. Signals for 4 were assigned in a similar manner.

2.3 X-ray Crystallography

Intensity data were collected at -100(2) °C on a Bruker APEX2 CCD area detector diffractometer with graphite monochromated Mo K α radiation (50kV, 30mA). The collection method involved ω - and ϕ -scans of width 0.5° and 1024x1024 bit data frames. Face indexed absorption corrections were carried out using XPREP [86]. All crystal structures were solved by direct methods. Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full matrix least-squares calculations based on F^2 . Hyrides bonded to Iridium in compounds **4** and **5** were placed in geometrically calculated positions (Ir-H distances fixed at 1.55 Å) as it was not possible to locate these atoms in the Fourier difference maps. Software used in this work were as follows: Data

collection: *APEX2* [87]; cell refinement and data reduction: *SAINT* [86]; program suite used to solve and refine structures: *SHELX-2014* [88]; molecular graphics: *PLATON* [89]; software used to prepare material for publication: *WinGX* [90] and *PLATON*. Crystal data and structure refinement for **1**, **3**, **4**, **5** and **6** are given in the supplementary information. Selected bond lengths and angles are given in Table 1 (**1** and **3**) and Table 2 (**3**-6).

3. Results and Discussion

The methoxy bridged complex $[Ir_2(\mu-OMe)_2(1,5-cod)_2]$ (1), first reported in 1965 by Robinson and Shaw [84], provides a valuable route to a potentially wide range of iridium(I) complexes in which cyclooctadiene and a chelating anionic ligand (L^L) or thiolate are bound to the metal [85, 92, 93]. The reaction of 1 with the ligand precursor HL^L or RSH in benzene, dichloromethane or diethyl ether tends to be rapid (complete within a few seconds) and gives methanol as the only side product. An early crystallographic study of 1 [91] extended only as far as a description of the unit cell. The structure of 1 (Fig. 1) is angular with the plane defined by Ir1, O1 and O2 displaced by 38.5(2) ° from the plane defined by Ir2, O1 and O2. The methoxy C-O bonds dip slightly towards the iridium atoms, with the projected C9-O1 bond axis lying at an angle of 4.0(6) ° with respect to the projected C10-O2 bond axis.

In toluene in the presence of two equivalents of diphenyltriazene per iridium **1** is converted to a complex formulated as $[Ir(\eta^1-N_3Ph_2)(HN_3Ph_2)(1,5-cod)]$ (**2a**) (Scheme 1) on the basis of a low temperature NMR study. The ¹H spectrum recorded at 198 K shows signals at 14.07 (NH), 7.93-6.89 (20 x ArH), 3.74 (4 x alkene H), 2.30 and 1.93 (8 x CH₂), all broadened as a result of dynamic processes. The NH hydrogen shows NOE interactions with the aromatic and alkene hydrogens, from which it would appear that a single Ph₂N₃H occupies a position in the coordination sphere of the metal, in a complex in which a triazenide ligand is attached to the metal via an η^1 bond. The ¹H signals at 7.93 and 7.53 (integrating for 8 *ortho* hydrogens) coalesce into a single broadened signal at 213 K (Fig. 2), indicating that whatever process is occurring affects all four phenyl groups equally. The equivalence (or near equivalence) of the alkene hydrogens does not extend to the alkene carbons, from which two broadened signals are obtained which differ in chemical shift by 2.5 ppm. The above evidence rules out the possibility of an η^2 bonded iridium(I) triazenide [Ir(η^1 -N₃Tol₂)(CO)(PPh₃)], reported by Bombieri and coworkers [4], has been structurally characterised and shown by ¹H NMR to exhibit fluxional behaviour. Palladium and platinum complexes having an η^1

bonded triazenide are also fluxional. A kinetic study of *trans*-[Pd(N₃Ar₂)(X)(EPh₃)₂] (X = Cl, Br; Ar = 4-C₆H₄CH₃, 4-C₆H₄OCH₃; E = P, As) and *cis*-[Pt(N₃Ar₂)(Cl)(PPh₃)₂] by Robinson and coworkers [17] provides evidence for a rapid N1-N3 interchange. An iridium triazene complex [Ir(Cl)(CO)₂(η^{1} -HN₃Tol₂)] reported by Connelly and coworkers [94] shows no fluxionality (CD₂Cl₂ solution) in the temperature range 20 - -80 °C, unlike its rhodium analogue.

The ¹H NMR spectrum of **2a** (~ 0.02 M in toluene, formed from **1** and two equivalents of Ph₂N₃H per iridium) at temperatures of 223 K or below shows no significant change over a period of several hours. At 300 K **2a** in the same solution is slowly (~ 50% in 90 minutes) converted into $[Ir_2(\mu-N_3Ph_2)_2(1,5-cod)_2]$ (**3**), which can be isolated as black crystals. In the absence of a second equivalent of Ph₂N₃H a more transient species $[Ir(N_3Ph_2)(1,5-cod)(L)]$ (**2b**) is likely to be formed, where L is solvent or methanol. The ¹H NMR spectrum of **3** in chloroform recorded at temperatures in the range 300 to 215 K shows evidence of fluxional behaviour (Fig. **3**). At 300 K a broad (~ 0.5 ppm wide) signal, integrating for 6 phenyl hydrogens, is found centred at 7.4 ppm and two broad alkene signals can be found at 4.15 and 3.80 ppm each integrating for four hydrogens. At 288 K the signal at 7.4 ppm begins to become resolved into two signals, clearly separated (7.8 and 6.9 ppm) at 277.5 K, at which temperature the two alkene signals coalesce, becoming resolved into three signals at 269 K. At 240 K the 6.9 ppm phenyl signal is broadened and is transformed into two signals (δ 7.6 and 6.7) at 230 K, at which temperature a signal at 7.3 ppm becomes broadened (giving two signals at 220 K) and four alkene signals are clearly resolved.

The structure of **3** (Fig. 4) has the two bridging triazenides holding the two iridium atoms in a conformation somewhat resembling the cyclohexane 'boat' geometry. The mean planes of the approximately square planar iridiums lie at an angle of 55.6(1) ° relative to each other, with the iridium atoms separated by 2.9925(3) Å. The two triazenides do not occupy identical positions in the structure. This is shown by the torsion angles C9-N1-N3-C15 and C29-N4-N6-C35 which differ by 9.7°. It would appear likely that a fluxional process reflected in the V.T. ¹H spectra arises from the inversion of the 'boat' conformation, permitted by rotation about the N-N bonds. Such a process would cause the alkene environments 1, 6, 21, 26 and 2, 5, 22, 25 to undergo exchange.

Crystalline products **4**, **5** and **6** (Scheme 2 and Figs. 5-7) are formed in moderate to good yield from the reaction of freshly prepared (less than 1 min from time of mixing) solutions of **1** and diphenyltriazene with triphenylsilane, triphenyltin hydride and pentafluorophenyl thiol respectively. ¹H NMR shows that **2a** in toluene solution is converted rapidly and quantitatively into **5** upon treatment with triphenyltin hydride. A noteworthy feature of the chemistry summarised in Scheme 2 is that the triphenylsilane-containing product **4** is stable in solution in the absence of an excess of

the free silane, unlike complexes containing isoquinoline carboxylate [92] or 8-oxyquinolinate [93] in place of triazenide. This might be viewed as evidence that the Ir(I) complex formed by dissociation of the silane, while stable in the case of the isoquinoline carboxylate and 8-oxyquinolinate ligands (complexes [Ir(O₂Clsoq)(cod)] and [Ir(80Q)(cod)]) is unstable in the case of the triazenide ligand, the much smaller 'bite' angle of 58-60° for the η^2 -bonded triazenide imposing distortions not readily accommodated in a nominally square planar structure. With C₆F₅SH a product **6** (Scheme 2) is obtained containing two pentafluorophenyl thiolates, indicating a probable second oxidative addition (of C₆F₅SH) accompanied by loss of H₂. There is no evidence (by 1H NMR) for a reaction between **2** and triphenylmethane.

The conversion of **2a** into **6** might proceed as follows. Although there is no direct evidence for the steps described precedents can be found. Oxidative addition of a single C_6F_5SH would be expected, from the evidence above, to give a product analogous to **4** and **5**. The most obvious first step in any further reaction would be the creation of a vacant coordination site, which could easily be achieved by the detachment of a triazenide nitrogen (to give an η^1 bonded triazenide) in what might be considered to be a rapid, reversible and ongoing process [17]. The vacant site would then allow the binding of C_6F_5SH as a neutral ligand. The hydrogen bound to sulphur could then migrate to the adjacent hydride forming a neutral H₂ ligand while the C_6F_5SH to which it was attached becomes anionic [95, 96]. Dissociation of H₂ followed by reattachment of the triazenide as a chelating ligand would give **6**. The reasons why such behaviour is not observed in the case of **4** and **5** would clearly be that SiHPh₃ and SnHPh₃ are far less willing to bind as neutral ligands, requiring the formation of a metal-EH (E = Si, Sn) three centre bond, rather than simple coordination via a lone pair, as with sulphur.

The geometry at iridium in **4-6** can be described as distorted octahedral, with relatively minor differences between the structures of **4** and **5**, the most prominent of these being in the Si-Ir-N3 and Sn-Ir-N3 bond angles, the latter being 4.6 ° smaller than the former, although Sn is the larger atom. Crystals of **4** and **5** differ in that those of **4** are chiral, containing only one enantiomer, while those of **5** contain both. Complex **6** crystallises on a crystallographic twofold axis. The two SC₆F₅ groups are equivalent as are the two PhN fragments. It should be noted that the differences that can be found between the structures of **4** and **5** are sufficiently small that most might be attributable to crystal packing forces. The iridium-carbon bonds are longer for the alkene positioned *trans* to E by approximately 0.11 Å (E = Si) and 0.08 Å (E = Sn) as compared with the alkene positioned *trans* to nitrogen. The iridium-nitrogen bonds are longer for N3 (positioned *trans* to H) by approximately 0.16 Å (E = Si) and 0.12 Å (E = Sn) as compared with the Ir-N1 distance (2.05 Å). These observations can be

rationalised in terms of the magnitude of the *trans* influence for H, SiPh₃ and SnPh₃ [97]. The Ir-N1-C15 bond angle $(150.0(5)^\circ, E = Si; 147.5(5)^\circ, E = Sn)$ is more than ten degrees larger than the Ir-N1-C9 bond angle $(137.4(5)^\circ, E = Si; 136.5(5)^\circ, E = Sn)$. This difference might be accounted for by the differing steric sizes of the hydride and equatorial alkene. In complex **6**, where there is a plane of symmetry, the Ir-N1(N1a)-C5(C5a) angle is 143.1(2)°, close to the midpoint between the values noted for **4** and **5** above.

4. Conclusion

The complex $[Ir(\eta^1-N_3Ph_2)(HN_3Ph_2)(1,5-cod)]$ (**2a**), formed in solution from $[Ir_2(\mu-OMe)_2(1,5-cod)_2]$ (**1**) and four equivalents of diphenyltriazene, has been characterised by low temperature NMR spectroscopy. The monodentate triazenide in the Ir(I) complex becomes bidentate in the Ir(III) complexes $[Ir(\eta^2-N_3Ph_2)(H)(SiPh_3)(1,5-cod)]$ (**4**), $[Ir(\eta^2-N_3Ph_2)(H)(SnPh_3)(1,5-cod)]$ (**5**) and $[Ir(\eta^2-N_3Ph_2)(SC_6F_5)_2(1,5-cod)]$ (**6**) (all characterised by X-ray crystallography) obtained from the reaction of solutions containing **1** and Ph₂N₃H with SiHPh₃, SnHPh₃ and C₆F₅SH respectively.

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Supplementary data

CCDC 1449956-1449960 contain the supplementary crystallographic data for structures listed in Table 3. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or email: deposit@ccdc.cam.ac.uk.

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Table 1. Selected interatomic distances (Å) and angles (°) for 1 and 3.

[Ir ₂ (OMe) ₂ (1,5-cod) ₂] (1)			
lr1-01	2.067(4)	lr1-lr2	3.1085(3)
Ir1-02	2.056(5)	lr1-01-lr2	97.52(19)
Ir2-01	2.067(5)	lr1-02-lr2	97.47(19)
Ir2-02	2.080(5)	01-lr1-02	74.71(18)
01-C9	1.418(7)	01-lr2-02	74.19(18)
O2-C10	1.406(8)		\mathbf{O}
[Ir ₂ (N ₃ Ph ₂) ₂ (1,5-cod) ₂] (3)			
lr1-N1	2.114(3)	N5-N6	1.303(5)
Ir1-N6	2.098(4)	Ir1-N1-N2	128.7(3)
Ir2-N3	2.094(4)	lr1-N6-N5	124.9(3)
Ir2-N4	2.145(3)	Ir2-N3-N2	123.0(3)
lr1-lr2	2.9925(3)	Ir2-N4-N5	126.2(3)
N1-N2	1.294(5)	N1-N2-N3	115.2(4)
N2-N3	1.308(5)	N4-N5-N6	115.8(4)
N4-N5	1.304(5)		
C			

Table 2. Selected interatomic distances (Å) and angles (°) for 4, 5 and 6.

Ir-N1	2.047(6)	N1-Ir-N3	58.4(3)
Ir-N3	2.213(6)	Ir-N1-N2	102.1(4)
Ir-Si	2.398(2)	Ir-N3-N2	94.1(4)
Ir-H	1.55	N1-N2-N3	105.2(6)
N1-N2	1.309(7)	Si-Ir-N1	92.2(2)
N2-N3	1.310(8)	Si-Ir-N3	89.02(18)
[Ir(N ₃ Ph ₂)(H)(SnPh ₃)(1,5-cod)] (5)			
Ir-N1	2.051(5)	N1-Ir-N3	58.0(3)
Ir-N3	2.175(6)	Ir-N1-N2	103.0(5)
Ir-Sn	2.6151(5)	Ir-N3-N2	96.0(4)
Ir-H	1.55	N1-N2-N3	103.0(5)
N1-N2	1.298(9)	Sn-Ir-N1	89.47(15)
N2-N3	1.324(8)	Sn-Ir-N3	84.45(15)
[Ir(N ₃ Ph ₂)(SC ₆ F ₅) ₂ (1,5-cod)] (C ₆ H ₆)(5)			
Ir-S	2.4545(8)	Ir-N1-N2	98.60(19)
Ir-N1	2.056(3)	N1-N2-N1a	103.1(3)
N1-N2	1.306(3)	S1-Ir-S1a	166.13(4)
N1-Ir-N1A	59.68(14)	S1-Ir-N1	86.82(7)
	1	1	1



Fig. 1. Molecular structure of [Ir₂(μ-OMe)₂(1,5-cod)₂] (**1**). ORTEP drawn at the 50% probability level.



Fig. 2. ¹H spectrum of $[Ir(\eta^1-N_3Ph_2)(HN_3Ph_2)(1,5-cod)]$ (**2a**) (aromatic region only) in toluene recorded at 223 K (a), 213 K (b) and 198 K (c).



Fig. 3. ¹H spectrum of [Ir₂(μ-N₃Ph₂)₂(1,5-cod)₂] (**3**) (aromatic and alkene region only) in chloroform recorded at 300 K (a), 288 K (b), 277.5 K (c), 269 K (d), 250 K (e), 240 K (f) and 220 K (g).



Fig. 4. Molecular structure of $[Ir_2(\mu-N_3Ph_2)_2(1,5-cod)_2]$ (**3**). ORTEP drawn at the 50% probability level.



Fig. 5. Molecular structure of $[Ir(\eta^2-N_3Ph_2)(H)(SiPh_3)(1,5-cod)]$ (4). ORTEP drawn at the 50% probability level.

SCRIF



Fig. 6. Molecular structure of $[Ir(\eta^2-N_3Ph_2)(H)(SnPh_3)(1,5-cod)]$ (5). ORTEP drawn at the 50% probability level.



Fig. 7. Molecular structure of $[Ir(\eta^2-N_3Ph_2)(SC_6F_5)_2(1,5-cod)]$ (6). ORTEP drawn at the 30% probability level.



The reaction of $[Ir_2(\mu-OMe)_2(1,5-cod)_2]$ with four equivalents of diphenyltriazene gives a product formulated as $[Ir(\eta^1-N_3Ph_2)(HN_3Ph_2)(1,5-cod)]$ which combines with SiHPh₃, SnHPh₃ and C₆F₅SH to give oxidative addition adducts and slowly dimerises in solution forming $[Ir_2(\mu-N_3Ph_2)_2(1,5-cod)_2]$. In as for the ¹H NMR spectrum (above) recorded from toluene solution at 198 K signals from the triazenide