Formation of the Novel Benzophenone Sila-acylhydrazonato Complex $(\eta^5\text{-}C_5Me_5)Cl_3\overline{Ta[OC(SiMe_3)N}\overline{N}CPh_2]$ following Addition of Diphenyldiazomethane to an η^2-Sila-acyl Ligand

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The η^2-sila-acyl complex $cp^*Cl_3Ta(\eta^2\text{-}COSiMe_3)$ ($cp^* = \eta^5\text{-}C_5Me_5$) (**1**) reacts rapidly with diphenyldiazomethane to form $cp^*Cl_3\overline{Ta\{OC(SiMe_3)N}\overline{N}CPh_2\}$ (**2**), the first characterized product of reaction between an η^2-acyl compound and a diazoalkane.

Our studies of the carbonylation of early transition metal silyl compounds[1] have led to the discovery of the unusually electrophilic η^2-sila-acyl complex $cp^*Cl_3Ta(\eta^2\text{-}COSiMe_3)$ ($cp^* = \eta^5\text{-}C_5Me_5$) (**1**), which readily binds Lewis bases at the sila-acyl carbon to produce adducts of the type $cp^*Cl_3Ta\{\eta^2\text{-}OC(L)SiMe_3\}$ (L = pyridine, PR_3).[1b,c] In further examination of the chemistry of (**1**), we have investigated reactions with other donor compounds. Here we report the first example of a reaction between an η^2-acyl and a diazoalkane, which affords a new complex containing the novel benzophenone sila-acylhydrazonato(1−)-*N*′,*O* ligand.

Combination of benzene solutions of (**1**) and Ph_2CN_2 (1 equiv.) at room temperature results in a rapid colour change from violet to dark orange. Following work-up of the reaction mixture, bright yellow crystals of diethyl ether-soluble (**2**) were isolated in 57% yield. Formation of a 1 : 1 adduct of (**1**) and Ph_2CN_2 was apparent from elemental analysis and n.m.r. spectroscopy† [equation (1)].

I.r. stretches assigned to the benzophenone sila-acylhydrazonato ligand occur at 1555 cm^{-1} ($\nu_{C=N}$) and 1210 cm^{-1} (ν_{C-O}). These bands shift to 1540 and 1182 cm^{-1} respectively when $cp^*Cl_3Ta(\eta^2\text{-}{}^{13}COSiMe_3)$-[^{13}C]-(**1**) is used to prepare [^{13}C]-(**2**). A shoulder at 1565 cm^{-1} in the i.r. spectrum of [^{13}C]-(**2**) is tentatively assigned to the $Ph_2C{=}N$ group. Presumably this absorption is masked in the unlabelled derivative. These data are comparable with those of the ketone hydrazonato complexes $\overline{Re(OCRN}\overline{N}CR'_2)OCl_2(PPh_3)_2$.[2] In [^{13}C]-(**2**) the $SiMe_3$ group appears as a doublet ($^3J_{CH}$ 1.9 Hz) in the ^{1}H n.m.r. spectrum. The ^{13}C n.m.r. shift of the TaOCSi carbon is in the range typically observed for sp^2 carbons bearing oxygen substituents.[3] Interestingly, the $Ph_2C{=}N$ resonance is split into a doublet with a substantial carbon–carbon coupling constant ($^3J_{CC}$ 9.5). A *J* value of this magnitude is typical of three-bond couplings found in aromatic systems (*e.g.* $J_{C2,C5}$ 8.6 Hz in iodobenzene[3]), and may reflect some degree of delocalization within the chelate ring.

$$cp^*Cl_3Ta(\eta^2\text{-}C(O)SiMe_3) + Ph_2C{=}\overset{+}{N}{=}\overset{-}{N} \longrightarrow cp^*Cl_3\overline{Ta{-}O{-}C(SiMe_3){=}N{-}N}{=}CPh_2 \quad (1)$$

An *X*-ray crystal structure analysis was performed in order to determine unambiguously the nature of the bonding of the sila-acylhydrazonato ligand in (**2**).‡ An ORTEP view of the molecule is provided in Figure 1. The ligand environment about tantalum may be regarded as pseudo-octahedral, with the centroid of the cp* ligand occupying one co-ordination site, and the N(2) atom *trans* to cp*. The bonding in the

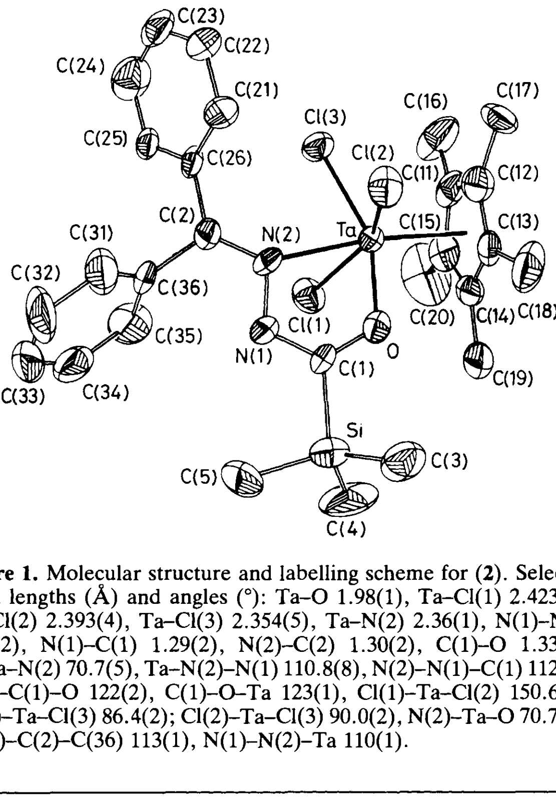

Figure 1. Molecular structure and labelling scheme for (**2**). Selected bond lengths (Å) and angles (°): Ta–O 1.98(1), Ta–Cl(1) 2.423(4), Ta–Cl(2) 2.393(4), Ta–Cl(3) 2.354(5), Ta–N(2) 2.36(1), N(1)–N(2) 1.43(2), N(1)–C(1) 1.29(2), N(2)–C(2) 1.30(2), C(1)–O 1.33(2); O–Ta–N(2) 70.7(5), Ta–N(2)–N(1) 110.8(8), N(2)–N(1)–C(1) 112(1), N(1)–C(1)–O 122(2), C(1)–O–Ta 123(1), Cl(1)–Ta–Cl(2) 150.6(2), Cl(1)–Ta–Cl(3) 86.4(2); Cl(2)–Ta–Cl(3) 90.0(2), N(2)–Ta–O 70.7(5), C(26)–C(2)–C(36) 113(1), N(1)–N(2)–Ta 110(1).

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† Satisfactory elemental analyses for C, H, N, and Cl. ^{1}H N.m.r. (300 MHz, [^{2}H$_6$]benzene, 20 °C): δ 0.16 (s, 9H, $SiMe_3$), 2.21 (s, 15 H, C_5Me_5), 7.00 (m, 6 H, phenyl), 7.56 (m, 2 H, phenyl), 7.75 (m, 2 H, phenyl). $^{13}C\{^1H\}$ N.m.r. (75.5 MHz, [^{2}H$_6$]benzene, 20 °C): δ −2.41 ($SiMe_3$), 12.76 (C_5Me_5), 126.9, 127.1 (*ortho* carbons, Ph), 129.4 (C_5Me_5), 129.7, 130.0 (*para* carbons, Ph), 131.3, 132.0 (*meta* carbons, Ph), 139.8, 142.5 (*ipso* carbons, Ph), 173.6 (TaOCSi), 177.4 ($Ph_2C{=}N$).

‡ *Crystal data* for (**2**): $C_{27}H_{34}Cl_3N_2OSiTa$, monoclinic, $P2_1/c$, a = 17.071(7), b = 11.008(4), c = 17.592(8) Å, β = 113.05(4)°, U = 3042(2) Å^3, Z = 4, D_c = 1.57 g cm^{-3}, $F(000)$ = 1424. Data were collected at 23 °C on a Nicolet R3m/μ automated diffractometer using Wyckoff scans (variable scan speed, 5—20°/min) and were corrected for absorption (μ = 41.3 cm^{-1}, Mo-K_α). Of 5857 reflections collected ($4° < 2\theta < 50°$), 5353 were independent, R(int) = 3.6%, and of these 2819 were considered observed [$F_o > 5\sigma(F_o)$] and used in the solution (Ta located from Patterson) and refinment (blocked cascade). All remaining nonhydrogen atoms were located and refined anisotropically. Hydrogen atoms were calculated and fixed in ideal positions [d(C–H) = 0.96 Å, U = 1.2 U_{iso} of attached C]. Phenyl rings fixed as rigid hexagons [d(C–C) = 1.395 Å]. R_F = 5.80%, R_{wF} = 5.75%, G.O.F. = 1.005, Δ(ρ) = 1.2 e Å^{-3} (1.1 Å from Ta). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

sila-acylhydrazonato ligand is best represented by the structure shown in equation (1). The C(1)–N(1) and C(2)–N(2) distances [1.29(2) and 1.30(2) Å, respectively] are in the region expected for carbon–nitrogen double bonds.[4] Distances and angles about C(1) show only a slight distortion from idealized sp^2 geometry. Distortions in the angles about C(2) are presumably due to steric interactions between one of the phenyl rings and Cl(3). The Ta–N(2) distance, 2.36(1) Å, is relatively long and therefore consistent with a dative interaction.[5]

In common with other Lewis bases such as pyridine (py) and phosphines, Ph_2CN_2 attacks the sila-acyl carbon atom of (**1**).[1c] In the formation of (**2**), however, a second donor atom is made available to co-ordinate to the metal and form the five-membered heterocycle. This implies that the Ta–C bond in adducts of the type $cp^*Cl_3Ta\{\eta^2\text{-}OC(L)SiMe_3\}$ may be readily broken by incoming ligand. The sila-acyl adduct (**2**) is inert towards exchange of Ph_2CN_2 with other Lewis bases (py or PMe_3, excess, $[^2H_6]$benzene, 1 day), presumably owing to the stability of the five-membered chelate ring. This behaviour contrasts with that observed for $cp^*Cl_3Ta\{\eta^2\text{-}OC(py)SiMe_3\}$, which undergoes facile pyridine exchange by an S_N1 pathway.[1c]

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