Reactivity of Tantalum η²-Iminoacyl Groups: Intramolecular Coupling, Reduction, and Dealkylation

Linda R. Chamberlain,[a] Ian P. Rothwell,*[a] and John C. Huffman[b]

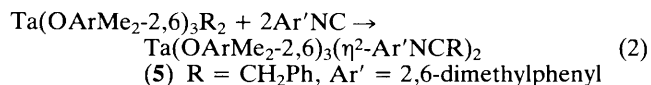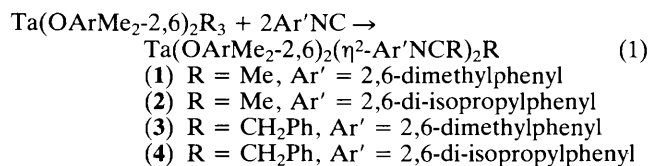[a] Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, U.S.A.
[b] Molecular Structure Center, Indiana University, Bloomington, Indiana 47405, U.S.A.

The reaction of arylisocyanides with a number of mixed alkyl, aryloxides of tantalum allows the isolation of the corresponding iminoacyl derivatives which can further react to give a range of products; the structures of the complexes obtained have been confirmed by X-ray diffraction.

One of the most widely studied and important organometallic reactions is the migratory insertion of carbon monoxide into metal–alkyl (and hydride) bonds.[1] However, it is the ensuing reactivity of the metal–acyl (or formyl) functional groups that determines the possible products that one can expect from the stoicheiometric or catalytic reduction of carbon monoxide by such systems.[2] We report here our initial findings on the structure and reactivity of the isoelectronic iminoacyl group bound to tantalum aryloxide metal centres. This work highlights the range of intramolecular processes that these functions can undergo.

The mixed alkyl, aryloxides Ta(OArMe$_2$-2,6)$_2$R$_3$ (OArMe$_2$-2,6 = 2,6-dimethylphenoxide; R = Me, CH$_2$Ph)[3] and Ta(OArMe$_2$-2,6)$_3$(CH$_2$Ph)$_2$[3] smoothly incorporate two equivalents of arylisocyanides (Ar'NC) to give the colourless bis-iminoacyl products (1)—(5) as shown in equations (1) and (2).

$$Ta(OArMe_2\text{-}2,6)_2R_3 + 2Ar'NC \rightarrow$$
$$Ta(OArMe_2\text{-}2,6)_2(\eta^2\text{-}Ar'NCR)_2R \quad (1)$$

(1) R = Me, Ar' = 2,6-dimethylphenyl
(2) R = Me, Ar' = 2,6-di-isopropylphenyl
(3) R = CH$_2$Ph, Ar' = 2,6-dimethylphenyl
(4) R = CH$_2$Ph, Ar' = 2,6-di-isopropylphenyl

$$Ta(OArMe_2\text{-}2,6)_3R_2 + 2Ar'NC \rightarrow$$
$$Ta(OArMe_2\text{-}2,6)_3(\eta^2\text{-}Ar'NCR)_2 \quad (2)$$

(5) R = CH$_2$Ph, Ar' = 2,6-dimethylphenyl

The spectroscopic properties of complexes (1)—(5) are consistent with the iminoacyl functions being η^2-bound.† In particular the observation of the Ar'NCR carbon resonating between δ 238 and 242 in the ^{13}C n.m.r. spectrum is
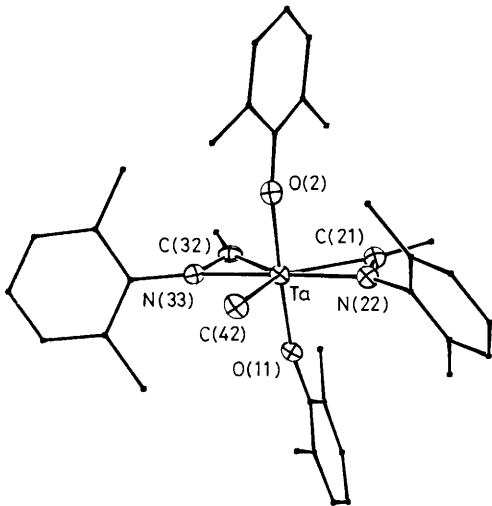
characteristic of this type of bonding.[4] An X-ray diffraction study of (1) was carried out and an ORTEP view of the molecule is shown in Figure 1.‡ It can be seen that the η^2-co-ordination of the iminoacyl groups is confirmed and the geometry about the metal can best be described as pentagonal bipyramidal with axial aryloxide ligands. The carbon and nitrogen atoms of the iminoacyl groups lie in a plane containing the Ta–R function which has no inserted groups, with the iminoacyl carbon atoms mutually cis. The ^{1}H n.m.r. spectrum of complex (1) is consistent with a similar structure being maintained in solution.† In particular, restricted rotation about the Ta–O–ArMe$_2$-2,6 bonds is seen, resulting in non-equivalent aryloxide methyl group resonances at low

Figure 1. Molecular structure of Ta(OArMe$_2$-2,6)$_2$(Ar'NCMe)$_2$Me (1). Selected distances (Å) and angles (°) are: Ta–O(2) 1.913(4), Ta–O(11) 1.938(4), Ta–N(22) 2.151(5), Ta–N(33) 2.165(5), Ta–C(21) 2.187(7), Ta–C(32) 2.200(6), Ta–C(42) 2.232(7), N(22)–C(21) 1.281(8), N(33)–C(32) 1.286(8), O(2)–Ta–O(11) 175.0(2), N(22)–Ta–N(33) 179.0(2), C(21)–Ta–C(32) 111.8(2).
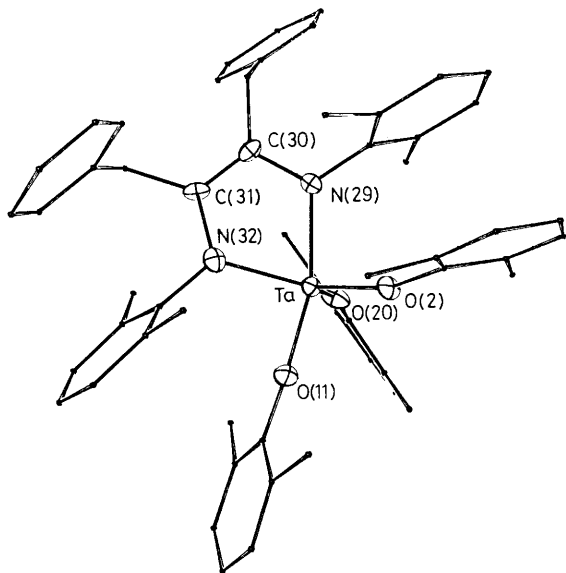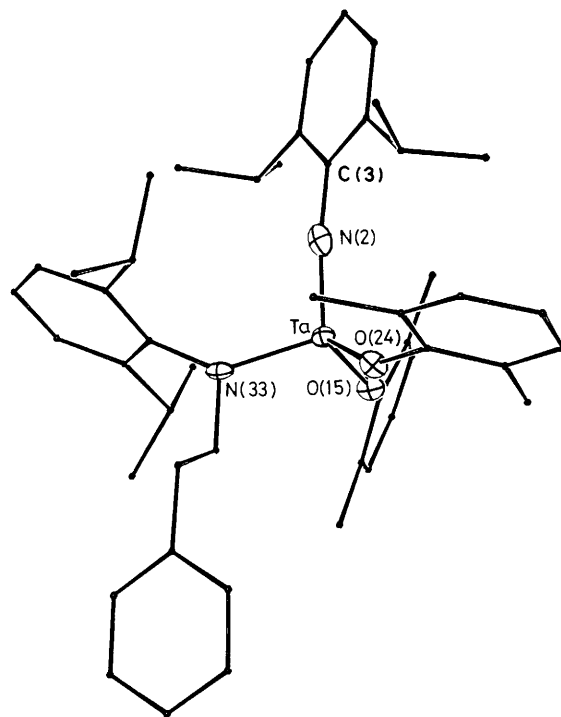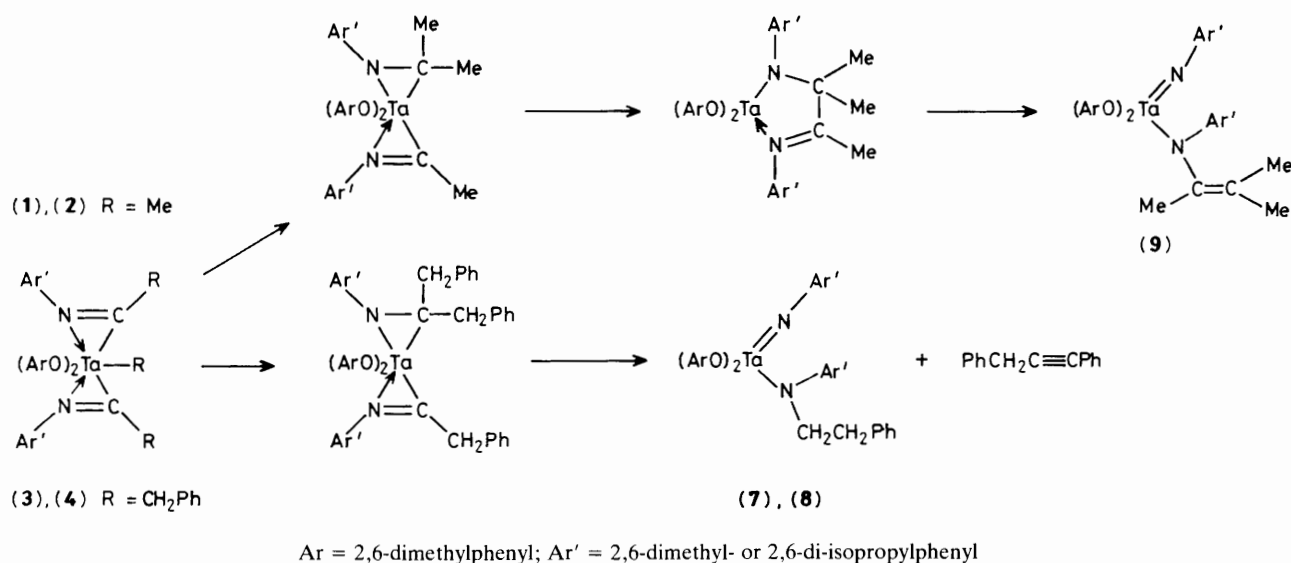

Figure 2. Molecular structure of Ta(OArMe$_2$-2,6)$_3${Ar'NC(CH$_2$Ph)=C(CH$_2$Ph)–NAr'} (6). Selected bond distances (Å) and angles (°) are: Ta–O(2) 1.898(5), Ta–O(11) 1.904(6), Ta–O(20) 1.880(6), Ta–N(29) 2.084(7), Ta–N(32) 2.041(7), N(29)–C(30) 1.409(11), N(32)–C(31) 1.432(10), C(30)–C(31) 1.352(11), N(29)–Ta–N(32), 74.6(3).

Figure 3. Molecular structure of Ta(OArMe$_2$-2,6)$_2$(=NAr')-(Ar'NCH$_2$CH$_2$Ph) (8). Selected bond distances (Å) and angles (°) are: Ta–O(15) 1.923(5), Ta–O(24) 1.916(5), Ta–N(2) 1.776(8), Ta–N(33) 1.951(7), Ta–N(2)–C(3) 172.0(6).

‡ *Crystal data:* (1), TaC$_{37}$H$_{45}$N$_2$O$_2$, M = 730.72, space group $P\bar{1}$, a = 10.881(2), b = 18.154(5), c = 9.188(2) Å, α = 99.07(1), β = 108.80(1), γ = 75.36(1)°, U = 1656.54 Å^3, Z = 2, D_c = 1.465 g cm^{-3}, λ(Mo-K_α) = 0.7106 9 Å. Of the 4358 unique intensities measured 3923 with $F_o > 3\sigma(F_o)$ yielded $R(F)$ = 0.0323, $R_w(F)$ = 0.0327.

(6), TaC$_{56}$H$_{59}$O$_3$N$_2$, M = 989.04, space group $P2/_1/c$, a = 18.869(8), b = 13.006(4), c = 21.971(9) Å, β = 119.46(2)°, U = 4694.60 Å^3, Z = 4, D_c = 1.399 g cm^{-3}. Of the 6121 unique intensities measured 4976 with $F_o > 3\sigma(F_o)$ yielded $R(F)$ = 0.0479, $R_w(F)$ = 0.0454.

(8), TaC$_{48}$H$_{61}$N$_2$O$_2$, M = 878.79, space group $P2_1/n$, a = 21.806(5), b = 19.568(6), c = 10.078(2) Å, β = 90.63(1)°, U = 4300.00 Å^3, Z = 4, D_c = 1.358 g cm^{-3}. Of the 5642 unique intensities, 4709 with $F_o > 2.33\sigma(F_o)$ yielded $R(F)$ = 0.419, $R_w(F)$ = 0.0439. The hydrogen atoms were located in (1) and (8) and refined isotropically. For (6) the positions of the hydrogen atoms were calculated and placed in fixed idealized [d(C–H) = 0.95 Å] positions for the final cycles of refinement. 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, 1986.

† *Selected spectroscopic data:* ^{13}C n.m.r. (C$_6$D$_6$, 30 °C); (1): δ 239.6; (2): 240.8; (3): 239.7; (4): 240.0; (5): 241.7 (all Ar'NCR). ^{1}H N.m.r. (C$_6$D$_6$, 30 °C); (1): δ 1.57 (s, Ta-CH_3), 2.48 (s, Ar'NCMe), 1.78 (s, NC$_6$H$_3$$Me_2$), 2.31 (broad, OC$_6H_3$$Me_2$). At −40 °C in C$_6D_5CD_3$ the OC$_6$H$_3$Me$_2$ groups split into two singlets, δ 2.28 and 2.35. (5): δ 4.63 (s, Ar'NCCH_2Ph), 1.83 (s, OC$_6$H$_3$$Me_2$), 2.28 (s, NC$_6H_3Me_2$). (6): δ 4.07 (s, CH_2Ph), 1.95 (s, OC$_6$H$_3$$Me_2$), 1.97 (s, NC$_6H_3$$Me_2$). (9): δ 1.46, 1.61, 3.45 (s, NCMeCMe_2), 2.30 (s, OC$_6$H$_3$$Me_2$), 2.14, 2.21 (s, NC$_6H_3$$Me_2$).

Ar = 2,6-dimethylphenyl; Ar' = 2,6-dimethyl- or 2,6-di-isopropylphenyl

Scheme 1. Possible pathways leading to imido, amido derivatives of tantalum from iminoacyl, aryloxide complexes.

temperatures. The similarity of the spectral data of complexes (1)—(4) indicates they are isostructural while for (5) we envisage a related structure with the unique metal–alkyl function which has no inserted groups being replaced by a metal–OArMe$_2$-2,6 function.

These complexes exhibit differing thermal reactivity. Complex (5) undergoes a clean thermal rearrangement to a new complex (6) no longer containing iminoacyl groups as indicated by ^{13}C n.m.r. studies. The product, confirmed by an X-ray diffraction study (Figure 2),‡ contains an ene-diamide (doubly reduced diazabutadiene) ligand formed by the intramolecular coupling of the η^2-iminoacyl groups. Similar reactivity has been demonstrated for these functions bound to group 4 metals.[4] However, it is interesting to note that the metallacycle in (6) is almost perfectly planar, in contrast to the significant bending observed in complexes of the type (ArO)$_2$M(Ar'NCR=CRNAr') (M = Ti, Zr).[4,5]

The benzyl complexes (3) and (4) thermally (toluene, 120 °C, 24 h) generate an organic product as well as new tantalum species (7) and (8) respectively in excellent yields. Structural studies show (8) to be a mixed imido, amido complex (Figure 3).‡ The amide function, Ta–N(Ar')CH$_2$CH$_2$Ph results from the hydrogenation of an iminoacyl group[6] by H$_2$, while the imido group represents the overall cleavage of the initial isocyanide reagent.[7] The organic product from thermolysis of both (3) and (4) has been identified (^{1}H n.m.r., i.r., and mass spectroscopy) as PhCH$_2$C≡CPh, benzylphenylacetylene.

In the case of the methyl complex (1), pale yellow solutions of this material darken slowly at 25 °C to produce after 7 days a deep purple solution of a new product (9). The spectroscopic data for (9) are consistent with its formulation as another imido, amido complex as shown (Scheme 1). The formation of the vinyl amido function has a precedent in the reported formation of vinyl alkoxides from the reaction of carbon monoxide with group 4[8] and group 5[9] metal alkyls, as well as the reaction of WMe$_6$ with Bu^{t}NC.[10]

We believe the different products formed from (1)—(4) are due to the presence of the extra alkyl group on the metal which can migrate to one of the co-ordinated η^2-imine groups to produce an η^2-Ar'NC(R)$_2$ ligand. The products can then be formed as shown in Scheme 1. The differing reactivities of the benzyl vs. methyl complexes are possibly due to steric effects.

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