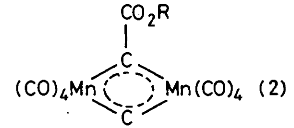
An α-Diazoalkylosmium Complex as a Carbyne-complex Precursor. Synthesis and *X*-Ray Crystal Structure of $[\overline{\mathrm{OsCl(I)(NO)(PPh_2C_6H_4C}}\mathrm{HCO_2Et)(PPh_3)}]$, the Product of an Intramolecular Carbyne Insertion Reaction

Mark A. Gallop, Tony C. Jones, Clifton E. F. Rickard, and Warren R. Roper*

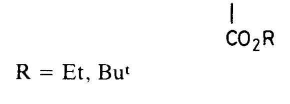
Department of Chemistry, University of Auckland, Private Bag, Auckland, New Zealand

The α-diazoalkylosmium complex $[\mathrm{OsCl(I)(NO)(CN_2CO_2Et)(PPh_3)_2}]$ loses N_2 to give the title complex and the formation of this metallacyclic compound, which has been structurally characterised by single crystal *X*-ray diffraction, is interpreted as arising from an intramolecular insertion reaction of an intermediate cationic carbyne complex, $[\mathrm{OsCl(NO)(\equiv C{-}CO_2Et)(PPh_3)_2}]\mathrm{I}$.

Decomposition of α-diazoalkyl-transition metal species would appear to offer an attractive route to metal-carbyne complex synthesis, *e.g.* equation (1). To date, α-diazoalkylmetal complexes have only been successfully used in the generation of metal bridging-carbyne complexes in two closely related reactions, with the isolated products arising from [2 + 2] cyclisation of intermediate mononuclear carbyne species: equation (2).[1,2]



(1)



(2)

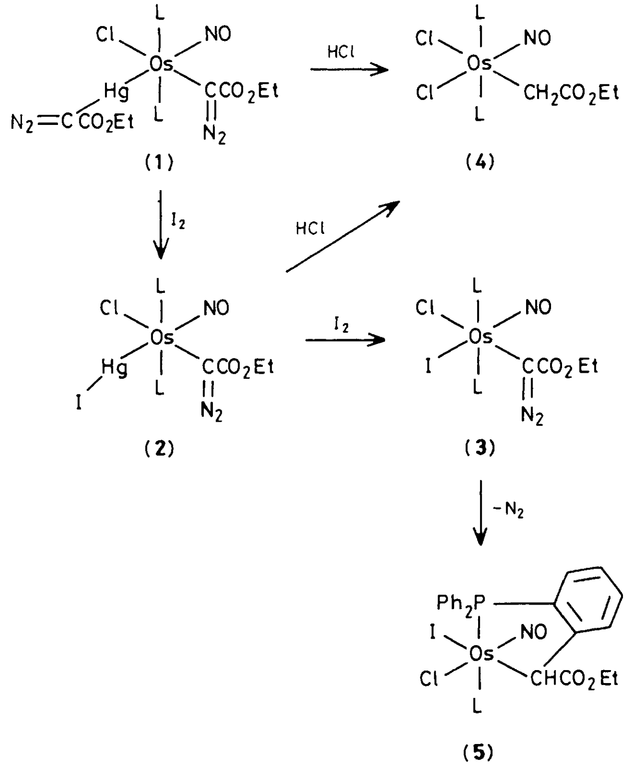
R = Et, Bu^t

The chemistry of stable α-diazoalkyl complexes of the d-block transition metals is undeveloped although the preparation and spectroscopic properties[3] of the palladium complexes $[\mathrm{PdCl(CN_2CO_2Et)(PPh_3)_2}]$ and $[\mathrm{Pd(CN_2CO_2Et)_2(PPh_3)_2}]$ have been described. The reactivity of these molecules has not been reported.

In this communication we report (i) the synthesis of osmium complexes containing the α-diazoalkyl ligand, $-\mathrm{C(N_2)CO_2Et}$, (ii) the carbyne-precursor properties of one of these compounds, and (iii) an *X*-ray crystal structure determination of (**5**), a complex formed by intramolecular carbyne insertion into an aryl C–H bond of a PPh_3 ligand.

Reaction between $[\mathrm{OsCl(NO)(PPh_3)_3}]$[4] and $[\mathrm{Hg(CN_2CO_2Et)_2}]$ yields the simple oxidative-addition product, $[\mathrm{OsCl(NO)(CN_2CO_2Et)(HgCN_2CO_2Et)(PPh_3)_2}]$, (**1**), [$\nu(N_2)$ 2070vs, 2049vs; ν(NO) 1755vs cm^{-1}]. A CH_2Cl_2 solution of (**1**) reacts with one molar equivalent of I_2 to afford $[\mathrm{OsCl(NO)(CN_2CO_2Et)(HgI)(PPh_3)_2}]$, (**2**), [$\nu(N_2)$ 2072vs; ν(NO) 1769vs cm^{-1}]. The parent diazomercury compound, $[\mathrm{Hg(CN_2CO_2Et)_2}]$, undergoes a related cleavage reaction with iodine.[5]

Treatment of (**2**) with further iodine results in cleavage of the Os–Hg bond, forming $[\mathrm{OsCl(I)(NO)(CN_2CO_2Et)(PPh_3)_2}]$, (**3**), [$\nu(N_2)$ 2061vs; ν(NO) 1842vs cm^{-1}]. On warming in an ethanol–benzene mixture, (**3**) extrudes nitrogen gas and the metallacyclic product (**5**), is isolated in good yield. These results are summarised in Scheme 1.



Scheme 1. α-Diazoalkyl complexes of osmium (L = PPh_3).

Yellow-orange, air-stable crystals of (**5**) suitable for *X*-ray analysis† were grown from CH_2Cl_2–EtOH using the isopiestic method and the structure is depicted in Figure 1. We propose that (**5**) is formed by an intramolecular insertion into the *ortho* C–H bond of the PPh_3 phenyl ring, of the carbyne carbon atom resulting from loss of N_2 from (**3**). One way in which the intermediate resulting from N_2 loss could be represented is as $[OsCl(NO)(\equiv CCO_2Et)(PPh_3)_2]I$. A related insertion reaction of a CHCl-carbene ligand has been proposed to explain the formation of the metallacycle in (**6**).[6] The stereochemistry of (**5**) as determined from the crystal structure has Cl *trans* to NO whereas (**1**), (**2**), and (**3**) are depicted in Scheme 1 as having Cl *cis* to NO assuming *cis*-addition of the mercury reagent.

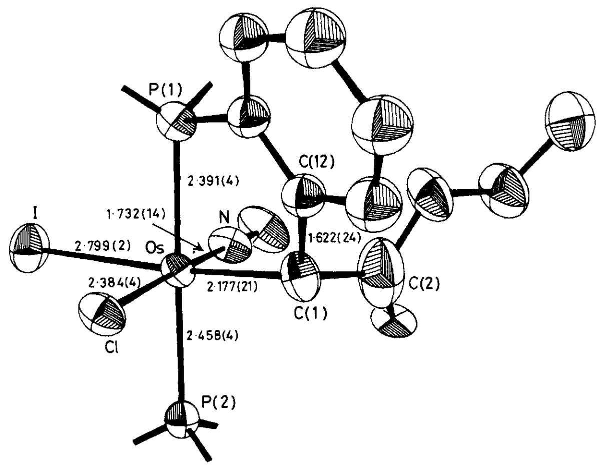


Figure 1. Molecular structure of (**5**), (phenyl rings omitted for clarity). Bond lengths are given in Å. Important angles are: P(1)–Os–P(2) 173.2(1), Os–C(1)–C(2) 110.0(1), Os–C(1)–C(12) 110.4(1), C(2)–C(1)–C(12) 114.6(2)°.

$$[\overline{OsCl(CO)_2(PPh_2C_6H_4C}HCl)(PPh_3)]$$
(**6**)

Reactions of (**1**) and (**2**) with another electrophilic reagent, HCl, are also summarised in Scheme 1. In both cases $[OsCl_2(NO)(CH_2CO_2Et)(PPh_3)_2]$, (**4**), is formed. This reaction contrasts with previously reported reactions of α-diazoalkylmetal complexes with Brönsted acids, which are typically characterised by protonation at C-α to give diazonium intermediates, N_2 loss, and anion attack at the resulting carbocation.[7] Protolytic cleavage of the Os–Hg bond, protonation at C-α, and subsequent hydride migration to this atom may explain the formation of (**4**) from compounds (**1**) and (**2**).

We thank Johnson Matthey Ltd. for a generous loan of OsO_4.

Received, 9th April 1984; Com. 502

References

1 W. A. Herrmann, *Angew. Chem., Int. Ed. Engl.*, 1974, **13**, 812.
2 W. A. Herrmann, M. L. Ziegler, and O. Serhadi, *Organometallics*, 1983, **2**, 958.
3 S. I. Murahashi, Y. Kitani, T. Hosokawa, K. Miki, and N. Kasai, *J. Chem. Soc., Chem. Commun.*, 1979, 450.
4 A. F. Hill, W. R. Roper, J. M. Waters, and A. H. Wright, *J. Am. Chem. Soc.*, 1983, **105**, 5939.
5 U. Schöllkopf, F. Gehart, M. Reetz, H. Frasnelli, and H. Schumacher, *Liebigs Ann. Chem.*, 1968, **716**, 204.
6 S. V. Hoskins, C. E. F. Rickard, and W. R. Roper, *J. Chem. Soc., Chem. Commun.*, 1984, preceding communication.
7 A. G. Brook and P. F. Jones, *Chem. Commun.*, 1969, 1324.

---

† *Crystal data* for (**5**): $C_{40}H_{34}ClNO_3OsP_2I$, M = 990.49, triclinic, space group $P\bar{1}$, a = 10.297(3), b = 20.490(4), c = 10.228(4) Å, α = 91.58(2), β = 115.90, γ = 100.92(2)°, U = 1891 Å^3, D_c = 1.74g cm^{-3} for Z = 2, $F(000)$ = 962, $\lambda(Mo\text{-}K_\alpha)$ = 0.71069 Å, $\mu(Mo\text{-}K_\alpha)$ = 42.07 cm^{-1}. 3915 Observed reflections [$F > 3\sigma(F)$] were collected on a CAD4 diffractometer. The structure was solved by Patterson and difference Fourier techniques and refined by full-matrix least-squares (all atoms anisotropic except phenyl carbon and hydrogen atoms) to $R = R_w$ = 0.047.

The atomic co-ordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.