Synthesis of Metal Carbene Complexes from Diazirines

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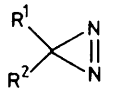
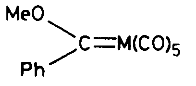
Reaction of methoxy(phenyl)diazirine (**1a**) with tungsten or chromium pentacarbonyl yields carbene complexes (**2a**) and (**2b**) by a mechanism not involving free carbene.

A variety of 3,3-disubstituted diazirines (**1**) are available and decompose thermally or by photolysis to yield carbenes which can be trapped by suitable alkenes.[1] Methoxy(phenyl)carbene is well known in its metal complex form[2] but few mononuclear metal carbenes have been prepared directly from *bona fide* carbene precursors. Diazo compounds displace tetrahydro-



(1a) R^1 = MeO, R^2 = Ph

(1b) R^1 = Br, R^2 = Ph



(2a) M = W

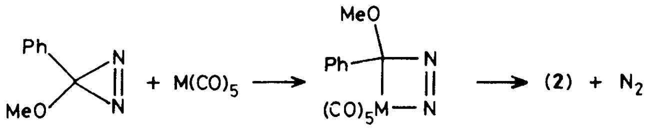
(2b) M = Cr

furan (THF) from (η^5-C_5Me_5)$Mn(CO)_2$THF to yield manganese carbenes *via* diazo complexes,[3] and bis(phenylthio)carbene is trapped with low efficiency by $M(CO)_5$THF (M = W, Cr) in reaction with $LiC(SPh)_3$.[4]

We now report the first synthesis of metal carbene complexes from diazirines. Photolysis of methoxy(phenyl)diazirine (**1a**)[5] in the presence of $W(CO)_6$ or $Cr(CO)_6$ at 0 °C (3 h, N_2 atm, G.E. Sunlamp) in hexane gave (**2a**) and (**2b**) in 13 and 8% isolated yields respectively.† Yields were based on bromo(phenyl)diazirine (**1b**) which was converted into the more sensitive (**1a**) on treatment with methoxide.[5] This reaction proceeded in less than 50% yield, so that the yields of carbene complexes relative to the proximate diazirine precursor (**1a**) were at least twice the cited values. The diazirine and the metal hexacarbonyl have similar u.v. maxima [λ_{max} (**1a**) 368 and 383 nm,[5] λ_{max} $M(CO)_6$ *ca.* 366 nm[6]], and the carbene complexes are photolabile, so that alternative thermal routes to (**2**) were sought.

The complexes $M(CO)_5$THF, formed on photolysis (366 nm, N_2 stream) of the hexacarbonyls in THF, are labile to substitution[7] and reacted in THF with (**1a**) in a dark reaction (0 °C, 3 h) to give (**2a**) and (**2b**) in 14 and 8% isolated yields. These yields were reduced to 4 and 2% at −20 °C. Either a reduced concentration of $M(CO)_5$ from dissociation or a lack of free carbene may have been responsible for the reduction.

To distinguish between a pathway involving the reaction of free methoxy(phenyl)carbene with $M(CO)_5$ or an insertion route involving the diazirine (Scheme 1), we required a reliable source of $M(CO)_5$. The most convenient was $M(CO)_5NH_3$, which could be purified readily and gave $M(CO)_5$ cleanly on photolysis ($\lambda > 370$ nm) at 0 °C of a pentane solution in a stream of nitrogen.[8] The $M(CO)_5$ fragment is relatively stable ($t_{\frac{1}{2}}$ *ca.* 30 min at 25 °C) and reacted (pentane, 0 °C for 2 h, or 25 °C for 1 h) with (**1a**) to yield (**2a**) and (**2b**) in 16 and 11% isolated yields. Reduction of the temperature to −20 °C afforded identical yields of complexes. This is consistent with the insertion route of Scheme 1, because the diazirine is thermally stable at −20 °C. Insertion of certain metal complexes into azirines, with subsequent rearrangement, is well established[9,10] and the cyclic intermediate proposed in Scheme 1 has many analogies in the mechanisms demonstrated by alkene metathesis.



Scheme 1

Various substituted diazirines are readily available[1] and further studies are underway to develop a general synthesis of metal carbene complexes.

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† Products (**2a**) and (**2b**) were isolated by chromatography on silica gel at 0 °C (degassed hexane), and identified by i.r., n.m.r., and t.l.c. comparisons wih authentic samples prepared by Fischer's route (ref. 2).