mode in reactions of V^{3+}.[11,12] It is interesting to note that $\Delta S^{\neq}$ is -11 ± 4 eu at 100° for $Fe(DMSO)_6{}^{3+}$ exchange and -16 eu for $Ni(DMSO)_6{}^{2+}$ DMSO exchange.[5] $V(DMSO)_6{}^{3+}$ should be especially interesting.

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Dihalocarbene Insertions into Optically Active R_3Si^*H with Retention of Configuration[1]

Sir:

Recently there has been much interest in carbene (or carbenoid) insertions into Si–X bonds in which X = H,[2] C (ring strained),[3] and Cl.[4] We wish to report the first stereochemical studies on such insertions, using optically active α-naphthylphenylmethylsilane, R_3Si^*H.[5] Specifically, the present work involved insertion of CCl_2 and CBr_2 using the appropriate organomercury compounds, trichloromethyl- and tribromomethylphenylmercury, $PhHgCX_3$.[6] The general procedure comprised refluxing a 200-ml benzene solution of the silane (40 mmol) and organomercury compound (40 mmol). Reaction times were 24 hr for $PhHgCCl_3$ and 4 hr for $PhHgCBr_3$. The phenylmercuric halide which formed was filtered, the solvent removed by distillation, and the crude product taken up in CCl_4 solvent. Unreacted R_3Si^*H in the crude product was converted to R_3Si^*OH by treatment with Cl_2 followed by hydrolysis of the Si–Cl bond, and the product was then passed through a column of silica gel for removal of the R_3Si^*-OH. This procedure gave $R_3Si^*CHX_2$ of good purity as determined by infrared and nmr spectra and analysis for C, H, and X. Using dextrorotatory R_3Si^*H the insertions proceeded as follows.

$$\underset{[\alpha]_D\ +35.0^\circ}{(+)\text{-}R_3Si^*H} + PhHgCX_3 \longrightarrow \underset{\substack{X\,=\,Cl;\ [\alpha]_D\ +21.0^\circ \\ X\,=\,Br;\ [\alpha]_D\ +14.3^\circ}}{(+)\text{-}R_3Si^*CHX_2}$$

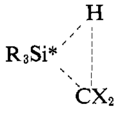
The problem of correlation of configuration between R_3Si^*H and $R_3Si^*CHX_2$ was overcome by preparation of the insertion products *via* independent syntheses involving reactions of known stereochemistry. The latter used organolithium reagents in coupling reactions with R_3Si^*Cl, a class of reactions known to proceed with inversion of configuration.[7] The dichloromethyllithium reagent was prepared in THF solvent by the general low-temperature method previously reported for α-chloroalkyllithium compounds.[8]

$$\underset{[\alpha]_D\ -35.2^\circ}{(-)\text{-}R_3Si^*H} + Cl_2 \xrightarrow{\text{retention}} \underset{[\alpha]_D\ +6.3^\circ}{(+)\text{-}R_3Si^*Cl} \xrightarrow[\substack{LiCHX_2 \\ -90^\circ}]{\text{inversion}} \underset{\substack{X\,=\,Cl;\ [\alpha]_D\ +22.6^\circ \\ X\,=\,Br;\ [\alpha]_D\ +13.8^\circ}}{(+)\text{-}R_3Si^*CHX_2}$$

Dibromomethyllithium was prepared by the reaction of dichloromethyllithium with dibromomethane[9] in THF solvent. Thus based on assignment of an inversion stereochemistry to the coupling reactions of $LiCHX_2$ with R_3Si^*Cl, (+)-$R_3SiCHCl_2$ and (+)-R_3Si^*-$CHBr_2$ have the same configuration as (+)-R_3Si^*H and *the insertion of CCl_2 and CBr_2 into the silicon–hydrogen bond proceeds with retention of configuration.* The solid $R_3Si^*CHCl_2$ from the coupling reactions was recrystallized up to constant rotation, $[\alpha]_D$ +24.4°, indicating optical purity. From this it appears that the insertion proceeded with a high degree of stereospecificity, ~93%.

The insertion products of R_3Si^*H and those obtained by coupling reactions of $LiCHX_2$ with R_3Si^*Cl had identical infrared and nmr spectra.

The present finding of a retention stereochemistry for the insertion reactions of CCl_2 and CBr_2 with R_3Si^*-H is certainly consistent with a three-center mechanism involving direct electrophilic attack of CX_2 on the silicon–hydrogen bond (I). It is interesting to note that a very similar mechanism (II) has been advanced previously[10] for the reactions of R_3Si^*H with X_2 (X = Cl or Br) which also proceed with retention of configuration. These reactions were postulated to involve electrophilic attack on R_3Si^*H by X^+. Transition states I and II both involve attack of electrophilic species on the silicon–hydrogen bond,[11] and both proceed with retention of configuration.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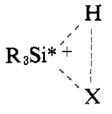
II

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(7) For recent numerous examples, see: L. H. Sommer, W. D. Korte, and P. G. Rodewald, *J. Am. Chem. Soc.*, **89**, 862 (1967).

(8) D. F. Hoeg, D. I. Lusk, and A. L. Crumbliss, *ibid.*, **87**, 4147 (1965). Our procedure employed −90° instead of −100° as reported.

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A Distinctly Bent Metal–Nitrosyl Bond. The Preparation and Structure of Chlorocarbonylnitrosylbis(triphenylphosphine)iridium Tetrafluoroborate, $[IrCl(CO)(NO)(P(C_6H_5)_3)_2][BF_4]$

Sir:

We wish to report the first accurately documented example of a distinctly bent M–N–O linkage in a metal nitrosyl complex and to present an explanation for this unusual mode of bonding.

Several small molecular species, including O_2,[1] SO_2,[2] and C_2F_4,[3] have been found to add to $IrCl(CO)(P(C_6H_5)_3)_2$, but there has been no report of the addition of NO to this system. We have found that the addition of NO^+ can be readily effected by adding a 50% excess of nitrosonium tetrafluoroborate, $NOBF_4$, to a hot saturated solution of $IrCl(CO)(P(C_6H_5)_3)_2$ in benzene under a nitrogen atmosphere, followed by the addition of sufficient anhydrous methanol to ensure homogeneity. A color change from yellow to violet occurs, and on cooling violet crystals of $[IrCl(CO)(NO)(P(C_6H_5)_3)_2][BF_4]$ (I) are formed. The infrared spectrum of I (Nujol mull) shows strong, sharp bands at 1680 and 2050 cm^{-1} which we ascribe to N–O and C–O stretches, respectively. *Anal.* Calcd for $[IrCl(CO)(NO)(P(C_6H_5)_3)_2][BF_4]$: Ir, 21.43; C, 49.54; H, 3.37; P, 6.90; N, 1.56; Cl, 3.95; B, 1.24; F, 8.47. Found:[4] Ir, 19.90; C, 49.64; H, 3.35; P, 6.82; N, 1.49; Cl, 3.58; B, 0.92; F, 8.57. The complex is found to be diamagnetic at room temperature by Faraday balance techniques.

The crystal structure of I has been determined by conventional heavy-atom methods from data obtained using Mo Kα radiation and a Picker four-circle automatic diffractometer.[5] The material crystallizes with four formula units in space group $C_{2h}{}^5$-$P2_1/c$ of the monoclinic system in a cell of dimensions a = 19.417 (7) Å, b = 9.965 (3) Å, c = 20.886 (8) Å, β = 117.70 (2)°; D_{calcd} = 1.677 g cm^{-3}; D_{obsd} (flotation) = 1.67 g cm^{-3}. The structure has been refined to a conventional R factor (on F) of 0.037 using 2410 reflections whose intensities are greater than three times their estimated standard deviations.

The geometry of the inner coordination sphere is shown in Figure 1. The Ir is five-coordinated, and the coordination polyhedron is best described as a distorted tetragonal pyramid, with *trans*-phosphorus, chlorine, and carbonyl in the basal plane and the nitrogen at the apex. The chlorine and carbonyl are slightly below the basal plane, the N–Ir–Cl and N–Ir–C angles being 101.3 (3)° and 97.4 (5)°, respectively. The bond lengths are shown in Figure 1. We have been able to demonstrate, by examination of the thermal parameters of the light atoms, that the NO is bonded through N rather than O and that the bent group is NO rather than CO.[6]

The bonding of the NO moiety to Ir is extremely interesting. While no direct comparisons can be made, the Ir–N bond length of 1.97 (1) Å is clearly long. Moreover, the Ir–N–O angle of 124 (1)° is very different from the near linearity reported for almost all other metal nitrosyl complexes. We suggest that the differences between I and other nitrosyl complexes are due to the ability of NO^+ both to accept and to donate electron pairs. In most nitrosyl complexes whose structures have been determined, the NO^+ group acts as a σ donor and gives a pair of electrons to an available empty metal orbital; the M–N–O group, therefore, is similar to the M–C–O group in metal carbonyls. These groups are essentially linear with the metal–ligand bond using an sp hybrid orbital on the donor atom. There is also considerable π back-bonding from the metal to the NO and CO groups as evidenced by the relatively short M–N and M–C bonds in such systems. In the case of I, however, there is no readily available metal orbital, and NO^+ acts as a σ acceptor, taking an electron pair from the weak base Ir(I). This requires sp^2 hybridization at the nitrogen atom with a lone pair occupying one hybrid orbital. This implies an Ir–N–O angle of 120°, in good agreement with the observed value of 124°. The expected weakness of metal–ligand π bonding accounts for the long Ir–N bond. Moreover, the value of ν_{NO} of 1680 cm^{-1} found in I is in the the range of 1500–1800 cm^{-1} found for organic and inorganic compounds of the type R—N═O, where R is a halogen, alkoxy, alkyl, or aryl group.[7] In these compounds the R—N═O linkage is bent.

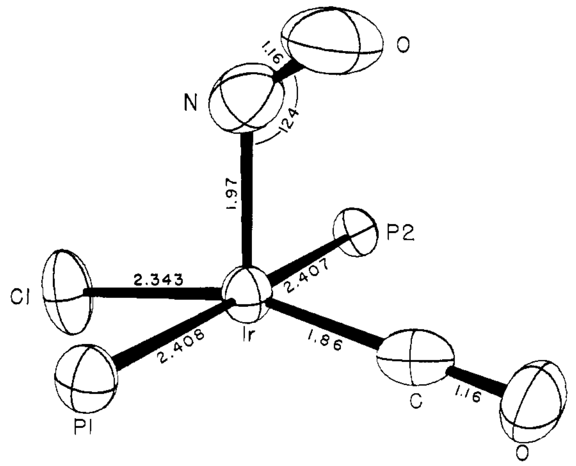

Figure 1. A perspective drawing of the coordination around Ir in $[IrCl(CO)(NO)(P(C_6H_5)_3)_2][BF_4]$.

In general, we believe that NO^+ will coordinate as an acceptor, or Lewis acid, in systems in which there is no available empty metal orbital. It is worthy of note that only one other metal nitrosyl complex, $Co(NO)(S_2CN(CH_3)_2)_2$ (II), has been shown by diffraction techniques to have a M–N–O angle which probably deviates greatly from linearity,[8] though this has been questioned.[9] We believe, however, that the NO^+ would probably act as a Lewis acid in II, since this is electronically and structurally similar to I, and we feel that the original structure determination may be correct, albeit somewhat inaccurate. We expect in general that groups which can act as either donors or acceptors may give different structures depending on their function. An example is SO_2, which forms a complex $IrCl(CO)(SO_2)(P(C_6H_5)_3)_2$ with a structure[10] completely analogous to that of I, with SO_2 acting as an acceptor, and a complex $[Ru(NH_3)_4Cl(SO_2)]Cl$ with the planar Ru–SO_2 structure[11] expected for SO_2 acting as a donor.

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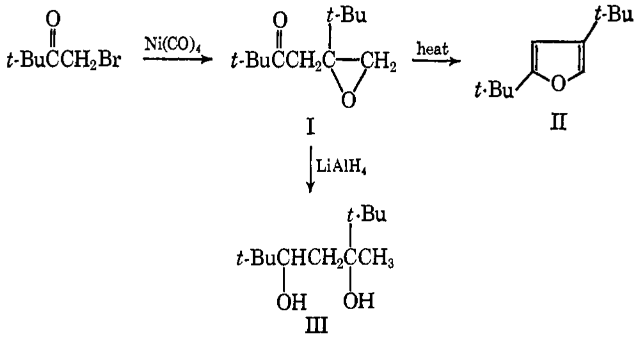
Direct Synthesis of β-Epoxy Ketones from α-Bromo Ketones and Nickel Carbonyl

Sir:

In general β-epoxy ketones can be prepared by epoxidation of β,γ-unsaturated ketones with perbenzoic acid.[1] However difficulty arises in the synthesis of β,γ-unsaturated ketones owing to easy rearrangement to the more stable α,β-unsaturated ketones. In the course of our studies on the reaction mechanism of furan formation between α-bromo ketones and nickel carbonyl in N,N-dimethylformamide (DMF)[2] we isolated β-epoxy ketones in good yield and find that this is a convenient method for the synthesis of β-epoxy ketones from α-bromo ketones using nickel carbonyl as a homogeneous reagent.

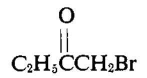
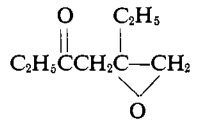
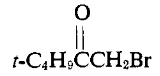
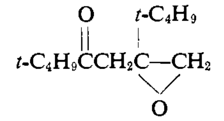
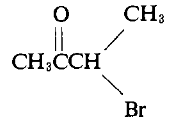
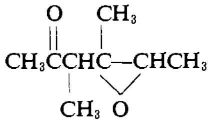
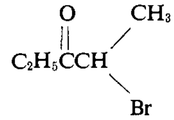
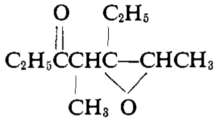
The reaction of 0.1 mol of an α-bromo ketone and 0.06 mol of nickel carbonyl in 30 ml of DMF was carried out under argon at 30° for 5 hr. The reaction mixture was then poured into dilute HCl aqueous solution and extracted with ether. The ether extract was washed with water and dilute sodium bicarbonate solution and then dried over anhydrous sodium sulfate. After removal of ether the residue was distilled and the product was characterized by infrared and nmr spectra, analysis, and chemical reactions. For example, the reaction of bromomethyl *t*-butyl ketone and nickel carbonyl gave a compound (I), bp 94° (9 mm), which showed a carbonyl band at 1735 cm^{-1} in its infrared spectrum. The nmr spectrum showed two singlet bands (9 H) for protons on two *t*-butyl groups at τ 9.10 and 8.89, and complex bands (4 H) for protons on two methylene groups at 7.1~7.7. *Anal.* Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.70; H, 11.15. This compound gave a negative ferric chloride test, showing the absence of enolizable protons, but gave a positive test with sodium thiosulfate solution, indicating the presence of an epoxide ring. When this compound is heated above 130°, dehydration occurred to give 2,4-di-*t*-butylfuran[3] (II), bp 184°. It has been reported that cyclohexenylacetone was converted into 2,3-tetramethylene-5-methylfuran by the dehydration of the epoxide intermediate with *p*-toluenesulfonic acid.[1] In our experiments it was found that the β-epoxy ketones can be used as unique starting materials for synthesizing furans. The formation of unsymmetrical furans by the reaction of α-bromo ketones and magnesium[3] or zinc[4] has recently been reported by two groups, but no attempts have been made to isolate epoxides in either case.

Upon reduction of I with lithium aluminum hydride in ether at 35° for 3 hr, a glycol (III), mp 84~86°, was obtained. The nmr spectrum showed two singlet bands (9 H) at τ 9.11 and 9.06, a singlet (3 H) at 8.80, two doublets (1 H) for methylene protons at 8.46 and 8.50, two doublets (1 H) for a tertiary proton, and a singlet (2 H) for alcoholic protons at 6.73 which disappeared by addition of D_2O. *Anal.* Calcd for $C_{12}H_{26}O_2$: C, 71.23; H, 12.95. Found: C, 71.37; H, 12.90. Formation of III by lithium aluminum hydride reduction of I is consistent with the general mode of rupture of primary linkage observed in substituted epoxide.[5]



The results of formation of β-epoxy ketones are given in Table I.

Table I. Formation of β-Epoxy Ketones from α-Bromo Ketones and Nickel Carbonyl

α-Bromo ketone	Product	% yield[a]
 $C_2H_5\overset{\overset{O}{\|}}{C}CH_2Br$		52
 $t\text{-}C_4H_9\overset{\overset{O}{\|}}{C}CH_2Br$		61
		70
		84

[a] Based on halide used.

These β-epoxy ketones are considered to be formed *via* aldol-type condensation between the nickel enolate and the α-bromo ketone, followed by elimination of $NiBr_2$, but a more detailed discussion of the mechanism will be given in a forthcoming paper.

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Received May 15, 1968

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