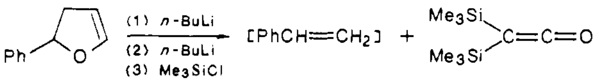
showed no evidence of isomerization of **9** to ketene **10** after 10 days. Thus, we conclude that the actual dianion is dilithioynolate **8** and not dilithioketene (**11**) and that the ketene products arise from a salt-promoted isomerization rather than a purely thermal rearrangement.[12,14]

Since a mixture of silylated ketene (and/or siloxyacetylene) and silylated dihydrofuran (e.g., **3** and **4**) is always obtained, we modified the starting material so as to make olefin extrusion more favorable. Use of 2-phenyl-2,3-dihydrofuran (**12**)[16] has the advantage of styrene extrusion rather than ethylene, and indeed sequential metalation of **12** with 2 equiv of *n*-BuLi followed by quenching with Me_3SiCl afforded ketene **6** in 65% yield uncontaminated by silylated dihydrofuran or styrene which is polymerized under these conditions.



12

6 65%

Acknowledgment. The support of this work by the National Science Foundation is gratefully acknowledged. We thank Professor Richard C. Larock for supplying us with the procedure for the synthesis of **12** before publication.

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(12) These observations call into question the sole report[13] of the generation of dilithioketene (**12**).

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(14) Theoretical calculations[15] place alkynols significantly higher in energy than the corresponding ketenes.

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(16) Although **12** is a known compound,[17] we have used a convenient synthetic procedure involving the $Pd(OAc)_2$ initiated reaction of dihydrofuran and iodobenzene.[18]

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(18) Private communication from Professor Richard C. Larock, who will soon publish this procedure.

A Trans Effect on Methyl Migration from Iridium(III) to Carbon Monoxide. The Influence of π Acceptor Ligands on the Methyl Migration Reaction

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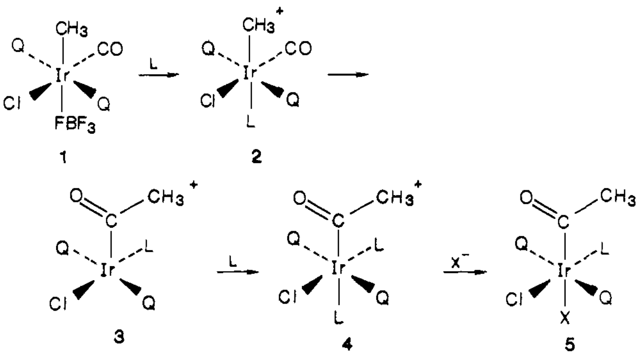
The migratory insertion of carbon monoxide into a metal–carbon bond has been intensively studied because of its significance in metal-catalyzed processes for forming carbon–carbon bonds.[1] Many aspects of the migration reaction including stereochemistry at carbon and the metal,[2] the effects of solvents[3] and incoming ligands, the migratory aptitudes of the migrating group, the acceleration of the migration reaction by Lewis acids[4] and oxidation–reduction,[5] and the characterization of unsaturated intermediates formed upon migration have been previously examined in great detail, but experimental studies on the influence of ligands on the primary migration step have not been reported. Berke and Hoffmann on the basis of molecular orbital calculations predicted in 1978 that π acceptor ligands L in the migrating plane should lower the activation energy for the primary migration step in the $Mn(CO)(CH_3)L$ system and that σ donor ligands should raise the activation energy,[6] but these predictions have not been verified. We report experiments which indicate that π acceptor ligands CO and isonitriles which are trans to the migrating methyl ligand do indeed promote migratory insertion and that σ donor ligands trans to the migrating methyl ligand do not promote migration.

Scheme I[a]



[a] Q is PPh_3. L is H_2O for **2A**. L is CO for **2B**, **3B**, **4B**, and **5B**. L is RNC for **2C**, **3C**, and **4C**. X is NCO for **5B-1** and NCS for **5B-2**. L is PhCN for **2D**. L is Cl^- for **2E**.

Addition of $(CH_3)_3OBF_4$ to *trans*-$[Ir(CO)Cl(PPh_3)_2]$ gave $[Ir(PPh_3)_2(CO)Cl(CH_3)BF_4]$, **1** [Anal. ($C_{38}H_{33}OP_2IrClBF_4$) C, H, Cl; IR ($cm^{-1}$, Nujol) 2067 (CO), 1060–1100 vs b (BF)]. Compound **1** in $CDCl_3$ rapidly reacts with water to give **2A** (L = H_2O) [(^1H NMR δ 0.82 (t, *J* = 4.7 Hz, 3 H), 4.9 (s, 2 H, H_2O), 7.5–7.8 (m, 30H, 6 Ph); $^{31}P\{^1H\}$ NMR δ 18.6 s; IR (cm^{-1}, $CDCl_3$) 2038 (CO), 1072–1110 vs b (BF), 3532, 1616 (OH)]. The triplet at 0.82 ppm is due to the coupling of the methyl hydrogen atoms with the two phosphorus atoms which as shown by the singlet ^{31}P NMR are trans to each other, and the assignment of the resonance at 4.9 ppm to water is verified by its immediate disappearance upon the addition of D_2O, CO, and isonitriles (see Scheme I). Addition of CO (30 psi) to **2A** initially gives **2B** characterized by ^1H NMR ($CDCl_3$) δ 1.08 (t, *J* = 6.8 Hz), IR (cm^{-1}, $CDCl_3$) 2097, 2071(CO), and gradual formation of singlet proton resonances at 1.21 and 1.25 ppm. These singlet proton resonances along with IR absorptions at 1732 and 1629 cm^{-1} are assigned to the acetylated species **3B** and **4B**. The neutral five coordinate phenylacetyl complex $[Ir(PPh_3)_2(PhCH_2CO)Cl_2]$, which is analogous to **3B** in which L is Cl, has been previously reported.[7] The structure for **3** is likely to be square pyramidal with the acyl ligand in the apical position analogous to the structure of $[Rh(PPh_3)_2Cl_2(PhCH_2CH_2CO)]$.[8] Reversible addition of CO to acylated 16-electron complexes analogous to **3** has been reported,[7] and the addition of anions X^- = NCO^- and NCS^- to **4B** led to the isolation of crystalline **5B-1** and **5B-2** [Anal. ($C_{40}H_{33}NO_3ClIrP_2$) C, H, N; IR (cm^{-1}, Nujol) 2218, 1335 (NCO), 2088 vs, 2059 sh, 1610 (CO). Anal. ($C_{40}H_{33}NO_2ClIrP_2S$) C, H, N; IR (cm^{-1}, Nujol) 2066 (NCS), 2028, 1612 (CO)]. Addition of ^{13}CO to **1** and CO to ^{13}CO labeled **1** established that the methyl carbon is bonded to the initially coordinated CO rather than the CO which is added.[9]

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(9) Addition of ^{13}CO to **2A** gave **3B** with ν(CO) shifted from 2067 to 2017 cm^{-1} and bands at 1732 and 1629 cm^{-1} unshifted. Addition of CO to ^{13}CO labeled **1** gave a spectrum with bands at 1697 and 1598 cm^{-1} shifted from 1733 and 1626 cm^{-1} in the unlabeled complex.

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Addition of 1,4-$CH_3OC_6H_4NC$ to **2A** in $CDCl_3$ gave immediate displacement of water to form **2C** (^1H NMR, δ 0.94 (t, J = 6.0 Hz 3 H) 3.79 (s, 3 H, OCH_3), and subsequent growth of a singlet resonance at 1.41 ppm with concomitant decay of the triplet at 0.94 ppm. This reaction mixture had IR absorption bands at 2189 (NC) and 1600 cm^{-1} (CO). The isonitrile in **4C** could not be replaced by anions, and instead several such complexes were isolated as crystalline materials [Anal. for $[Ir(PPh_3)_2(CH_3CO)Cl(CH_3C_6H_4NC)_2]BF_4$ ($C_{54}H_{47}N_2OClIrP_2BF_4$) C, H, N; IR (cm^{-1}, Nujol) 2211, 2181 (NC), 1610 (CO), 1051–1087 (BF). Anal. for $[Ir(PPh_3)_2(CH_3CO)Cl(PhCH_2NC)_2]BF_4$ ($C_{54}H_{47}N_2OClIrP_2BF_4$) C, H, N; IR (cm^{-1}, Nujol) 2254, 2223, (NC), 1606, 1054–1090 (BF). Anal. for $[Ir(PPh_3)_2(CH_3CO)Cl(ClC_6H_4NC)_2]BF_4$ ($C_{52}H_{41}OBCl_3F_4IrP_2$) C, H, N; IR (cm^{-1}, Nujol) 2178, 2208 (NC), 1608 (CO), 1030–1090 (BF)].

The methyl migration reaction promoted by the addition of isonitrile was found to be first order in **2C** and independent of isonitrile concentration.[10] The rates of migration with 1,4-substituted benzene isonitriles are not highly dependent on electronic factors; however, the migration rates were slower with benzyl isonitrile and 2,6-diisopropylbenzene isonitrile.

Addition of benzonitrile to **2A** in $CDCl_3$ leads to displacement of water and formation of **2D** (NMR δ 1.11 (t, 5.5 Hz)) and very slow transformation to migrated products **3D** and **4D**. σ donor ligands which were added to **1** which did not lead to migration of the methyl ligand from Ir to CO gave complexes **2** with ν(CO) shifted from 2038 cm^{-1} to the following frequencies (cm^{-1}): Et_3P, 2049; Ph_3PO, 2041; py, 2044; $(CH_3)_2S$, 2047; CH_3CN, 2055; Ph_3As and Ph_3P, 2040; and *p*-anisidine, 2055. Neutral derivatives of **2** where L is an anionic ligand which have been previously reported by Strope and Shriver[11] similarly do not undergo the methyl migration reaction. For example, treatment of the neutral complex **2E** (where L is the chloride anion) in benzene with 20 psi CO for 20 h did not give a methyl migrated product. Weaker π acceptor ligands such as $P(OPh)_3$, $P(OMe)_3$, or dimethyl acetylenedicarboxylate were found not to promote the methyl migration.

The promotion of methyl migration by the π acceptor CO and isonitrile ligands, but not by σ donor ligands, observed in this study is in accord with the calculations of activation energies for methyl migration by Berke and Hoffmann.[6] Complexes **2B** and **2C** with CO and isonitrile ligands trans to the migrating methyl ligand had CO stretching frequencies in the 2068–2077 cm^{-1} region, whereas complexes with σ donor ligands trans to the methyl ligand had CO frequencies in the 2038–2060-cm^{-1} region. In addition to exerting a trans labilization on the migrating methyl ligand, the π acceptor ligands also increase the susceptibility of the CO ligand to nucleophilic attack.[12] Interestingly, organophosphines which promote migration in the 16-electron Pt(II) system[13] do not appear to promote methyl migration in the 18-electron Ir(III) system.

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Supplementary Material Available: Experimental details and analyses (2 pages). Ordering information is given on any current masthead page.

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[10] The rates of migration were determined by measuring the decrease in absorbances of the CO stretching bands of the isonitrile complexes **2C** at 2074 cm^{-1} in dichloromethane at 25 °C. The rate constants ($\times 10^3$ s) observed for the 1,4-X benzene isonitrile complexes were for X = F, 8.6; X = Cl, 7.8; X = H, 8.8; X = CH_3, 8.5; X = CH_3O, 8.3; for $PhCH_2NC$, 3.5; and for 2,6-diisopropylbenzene isonitrile, 2.2.

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UV-Laser Photochemistry: Diffusion-Controlled Trapping of Cyclic 1,3-Diradicals by Molecular Oxygen. Conformational Effects on Triplet Lifetimes

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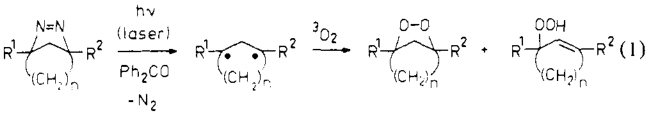
Oxygen trapping of triplet diradicals, generated via benzophenone-sensitized laser photolyses of azoalkane precursors has provided an effective tool for estimating lifetimes of such transient species, especially with localized radical centers such as the cycloalka-1,3-diyls **1** (eq 1).[2] In view of the lack of chromophores in the near UV–vis region, such diradicals are "invisible" in the more usually employed time-resolved laser flash spectroscopic detection.[3] Consequently, the oxygen-trapping method constitutes a complementary and useful extension, which permits probing such subtle features as conformational effects[4] in intersystem crossing processes.



1

1a ($R^1 = R^2 = H$; $n = 2$) **1b** ($R^1 = R^2 = Me$; $n = 2$)
1c ($R^1 = R^2 = H$; $n = 3$) **1d** ($R^1 = H$; $R^2 = Me$; $n = 3$)
1e ($R^1 = R^2 = Me$; $n = 3$)

For assessing the absolute triplet lifetimes in the oxygen-trapping method (competition kinetics), a critical parameter is the rate constant k_t for oxygen trapping (eq 2). Diffusion control

$$1/X_P = 1/[1 - X_H] = 1/T_f + 1/(k_t \cdot \tau_T \cdot [O_2]) \qquad (2)$$

X_P = mole fraction of peroxide (trapped product)

X_H = mole fraction of hydrocarbon (untrapped product)

$T_f = k_t/(k_t + k_c)$, the trapping factor

k_t = rate constant for oxygen trapping

k_c = rate constant for oxygen-catalyzed intersystem crossing

$\tau_T = 1/k_{ISC}$, the triplet lifetime

k_{ISC} = rate constant for intersystem crossing

was assumed[2] to estimate k_t for the cyclopenta-1,3-diyl (**1a**), as shown in (eq 3),[2] where the $^4/_9$ factor is the spin-statistical correction.[5] On one hand, free radicals react with $^3O_2$ at diffusion rates[6] and on the other hand the rate data available from time-

$$k(O_2) = k_t + k_c = (^4/_9) \cdot k_{diff} \qquad (3)$$

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[5] For the reaction of two triplets only the singlet and the three triplet encounter complexes lead to products, whereas the five quintets are dissociative.

0002-7863/87/1509-7570$01.50/0