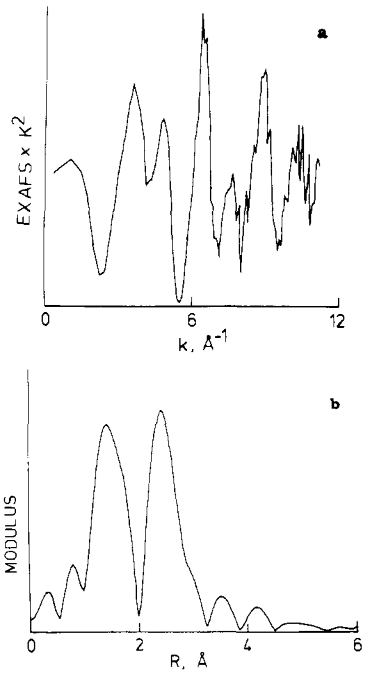

Figure 1. EXAFS data for electrochemically generated 10 mM $[Fe(CN)_6]^{4-}$ solution: (a) EXAFS spectrum after background subtraction and multiplication by k,[2] (b) Fourier transformation of weighted EXAFS spectrum.

increases significantly in absorptivity upon reduction to the Fe(II) complex. The energies of the inflection points are $K_3Fe(CN)_6$ solid, 7127.77 (2) eV; 10 mM $[Fe(CN)_6]^{3-}$ solution, 7127.60 (7) eV; $K_4Fe(CN)_6{\cdot}2H_2O$ solid, 7126.82 (11) eV; 10 mM $[Fe(CN)_6]^{4-}$ solution, 7126.98 (4) eV, where the number in parentheses is the estimated error in the last digit. Ten EXAFS spectra were recorded and averaged for each oxidation state. The EXAFS was extracted[7] from the total absorption spectrum by use of a cubic spline routine, and the EXAFS component due to the carbon atoms was isolated by Fourier filtering with a window of 1.0–2.0 Å in distance (R) space. Phase shift and amplitude parameters, obtained empirically from fits to $K_3Fe(CN)_6$ or $K_4Fe(CN)_6{\cdot}2H_2O$ solids, were used to fit data for the ferricyanide and ferrocyanide solutions over a k range of 4–10 $Å^{-1}$.

The extracted EXAFS (multiplied by k^2) is shown in Figure 1a for the ferrocyanide species. The complex EXAFS pattern displays a beat phenomenon arising from summation of sine waves due to backscattering contributions from carbon and nitrogen atoms where the large contribution from the latter results from the colinearity effect.[8] The Fourier transform of the EXAFS data into R space, illustrated in Figure 1b, displays two major peaks with the first (1–2 Å) due to carbon atoms and the second (2–3 Å) due to nitrogen atoms.

The results of single-shell fits using parameters from $K_3Fe(CN)_6$ solid are, for Fe(II), d = 1.97 Å and N_C = 7.4, for Fe(III), d = 1.94 Å and N_C = 6.8. Since coordination numbers (N_C) normally are determined to only 20% accuracy by EXAFS analysis, the N_C values are indistinguishable from those of a compound having coordination number of 6. On reduction from Fe(III) to Fe(II), the Fe–C bond length increases by 0.03 Å. This is the first direct observation of these bond-length changes[9] for the solution species. In the past, the evaluation of electron-transfer theories has depended on the use of crystallographic bond distances, which can vary over a wide range for a single oxidation state due to differences in counterion and degree of hydration. For the ferricyanide/ferrocyanide system, the variation in crystallographic bond lengths within the Fe(II) species[10-15] (10 Fe(II)–C bonds, max = 1.956, min = 1.896, mean = 1.914 (17) Å) and also for the Fe(III) moieties[16-20] (16 Fe(III)–C bonds, max = 1.945, min = 1.910, mean = 1.929 (9) Å) obscures the oxidation-state dependence in the Fe–C bond distance, so determination of the solution-phase bond lengths is highly desirable.

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Directed Cleavage of Carbon–Carbon Bonds by Transition Metals: The α-Bonds of Ketones

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Recently, remarkable progress has been made in the activation of carbon–hydrogen bonds by homogeneous metal complexes.[1] Less is known about the activation of simple, unstrained carbon–carbon bonds by soluble metal species.[2] Two factors would seem to disfavor C–C activation. The first is accessibility. While spherical species such as Fe^+ (in the gas phase)[3] or H^+ (in superacids)[4] can react preferentially with hydrocarbon C–C framework bonds, nonspherical reactive intermediates (such as CH_2) normally react with the peripheral C–H bonds. Thus, any sterically demanding species reactive enough to insert into a C–C bond will probably be intercepted by C–H bonds.[5] The second

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(5) This may not be an insurmountable problem with metal complexes. Since alkyl metal hydrides tend to be less stable than metal dialkyls, conditions may exist under which products from rapid reversible C–H activation are slowly drained off into metal dialkyls formed essentially irreversibly.

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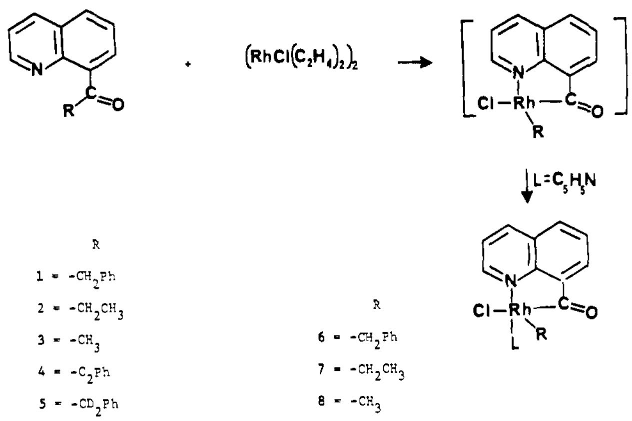
Scheme I



R
1 = $-CH_2Ph$
2 = $-CH_2CH_3$
3 = $-CH_3$
4 = $-C_2Ph$
5 = $-CD_2Ph$

R
6 = $-CH_2Ph$
7 = $-CH_2CH_3$
8 = $-CH_3$

problem with C–C activation is thermodynamics. By some estimates the oxidative addition of carbon–carbon bonds is endothermic by approximately 25 kcal/mol.[6] However, other estimates for metal–carbon bond strengths would just allow metal insertion into unstrained carbon–carbon bonds to be exothermic.[7] Metal complexes do insert into C–H bonds, and since C–C bonds are weaker than C–H bonds, one expects C–C bond insertion to be exothermic if a metal–carbon bond is weaker than a metal–hydride bond to the same extent that a C–C bond is weaker than a C–H bond. One complication with this analysis is the unknown effect of differing groups (in this case, carbon vs. hydrogen) on the strengths of other ligand–metal bonds in the complex.

We have looked for examples of directed insertion of metals into carbon–carbon bonds which would be analogous to directed carbon–hydrogen bond cleavage (the cyclometalation reaction).[8] In particular we have investigated 8-quinolinyl alkyl ketones (**1**–**3**) as ligands.[9] These have several advantages. Since five is the favored cyclometalation ring size, the metal, upon coordination to nitrogen in ligands **1**–**3** will be directed only to an α-ketone C–C bond. For C–H activation to compete, 6-membered rings would have to be generated. In addition, the α-ketone bond is slightly weaker than other carbon–carbon single bonds.[10] Thus, these ligands should overcome some of the problems with C–C bond activation mentioned above. We have shown previously that 8-quinolinyl acetylenic ketones (**4**) react with $RhCl(PPh_3)_3$ to give acylrhodium(III) acetylides.[11] However, the α-bonds of acetylenic ketones are quite reactive, being cleaved by nucleophiles such as NaOH.[12] The more representative α-ketone carbon–carbon bonds of ligands **1**–**3** do not react with NaOH nor do they oxidatively add to $RhCl(PPh_3)_3$.

In contrast, the ketone **1**[13] does react within minutes with a suspension of $[(C_2H_4)_2RhCl]_2$ in benzene at room temperature with loss of C_2H_4 to give an insoluble chlorine-bridged polymer,[14] which can be solubilized by pyridine to give the acylrhodium(III) benzyl complex **6**[15] (Scheme I). Although five-coordinate in solution[16] **6** crystallizes out in the presence of excess pyridine as the six-coordinate species whose structure is shown in Figure 1.[17] Given the strong trans influence of the benzyl group (Rh–N3 is 0.13 Å longer than Rh–N2) it is undoubtedly the pyridine trans to CH_2Ph that is lost in solution. Another interesting feature of the structure is the short rhodium–acyl bond length of 1.949 (4) Å. Other examples of rhodium(III) acyl bond lengths from highly refined structures are in the range 1.97–2.06 Å.[17] If the rhodium–carbon bond in the chelate ring is unusually strong, this would provide an additional driving force for carbon–carbon bond cleavage in ligands **1**–**5**.

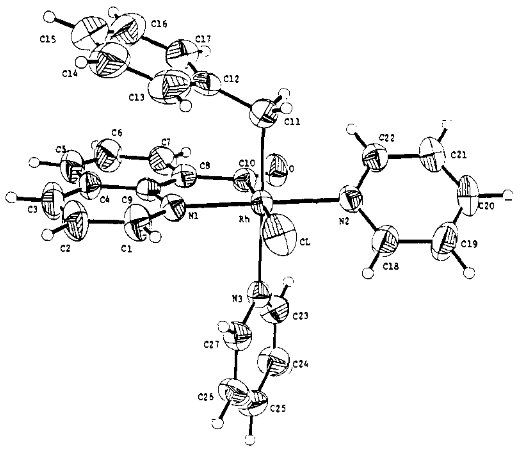


Figure 1. Molecular structure of **6**. Hydrogen atoms are at calculated positions. Selected distances (Å): Rh–Cl 2.545 (1), Rh–N1 2.042 (3), Rh–N2 2.093 (3), Rh–N3 2.221 (3), Rh–C10 1.949 (4), Rh–C11 2.103 (5).

Carbon–carbon bond cleavage occurs prior to solubilization by pyridine since treatment of the chlorine-bridged polymer (as well as **6**) with a stoichiometric amount of Br_2 generates benzyl bromide. Both **2** and **3** react with $[(C_2H_4)_2RhCl]_2$ in a similar manner (at 90 °C in benzene in a screw-cap vial overnight) to give **7** or **8**, respectively.[19] Bromine gives ethyl or methyl bromide from **7** or **8** as with **6**. Compound **7** can be made by an alternate route from $[(C_2H_4)_2RhCl]_2$, 8-quinolinecarboxaldehyde, and pyridine, and **7** made in this way has been subjected to single-crystal X-ray analysis.[20] It appears these complexes arise from direct oxidative addition into the α-ketone carbon–carbon bond. Reaction of **5** gave a product that had lost no deuterium. If prior C–H activation had occurred, the resulting rhodium hydride should have been trapped by ethylene[20] leading to either ethylation or H–D exchange in the ligand. In preliminary experiments with a range of 8-quinolinyl ketones and $[(C_2H_4)_2RhCl]_2$, we have yet

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(13) All new compounds gave satisfactory C, H, and N elemental analyses.

(14) Formed in quantitative yield, the measurement of gas evolved shows both ethylenes are lost. IR (Nujol) 1650, 1630, 780 cm^{-1}.

(15) IR (Nujol) CO 1625 cm^{-1}. ^1H NMR ($CDCl_3$, 250 mHz, ppm relative to Me_4Si) 10.28 (d, J = 5 Hz, 1 H, quinoline C-2) 6.5–6.3 (m, 5 H, Ph) 3.81 (d of d, J = 7.8, 3.6 Hz, 1 H one diastereomeric CH_2Ph) 2.83 (d of d, J = 7.8, 2.8 Hz, 1 H, other CH_2Ph); ^{13}C NMR (101 mHz) 22.2 (d, J_{Rh-C} 23.6 Hz).

(16) By NMR integration of the bound pyridine vs. quinoline resonances and by molecular weight determination by vapor-phase osmometry of **7** ($CHCl_3$ solution, found 402, calcd 402.7).

(17) Compound **6** was recrystallized from CH_2Cl_2–hexane–pyridine, the yellow-orange crystals were assigned to the monoclinic space group $P2_1/n$. Unit cell parameters were found to be a = 10.101 (3) Å, b = 16.476 (3) Å, c = 14.179 (2) Å, β = 93.888 (18)°, Z = 4. 2531 unique reflections were measured with Mo K_α radiation on a Nicolet $R3_m/E$ diffractometer. The structure was solved using the SHEXTL series of programs with the heavy atom located with the TRAN subroutine and least-squares refinement with anisotropic temperature factors for all non-hydrogen atoms. The final R_w based upon F^2 was 3.21% with no significant peaks in the final Fourier difference map. Hydrogen atoms were included at calculated positions and constrained to ride with the appropriate carbon atom.

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(19) Both **2** and **3** initially gave insoluble chlorine-bridged polymers, which were formed in quantitative yield. Elemental analyses of those solids corresponded to one rhodium, one chlorine, and one quinoline ligand. If freshly prepared $[(C_2H_4)_2RhCl]_2$ was used, these polymers dissolved upon addition of pyridine without a residue to give spectroscopically pure **7** or **8**. **7**: IR (Nujol, cm^{-1}) 1640. ^1H NMR 2.1 (m, J = 7, 6, 2 Hz, one diastereotopic CH_2), 1.7 (m, J = 7, 6, 2 Hz, other diastereotopic CH_2), 0.3 (t, J = 7 Hz, 3 H, CH_3); ^{13}C NMR 234 (d, J_{Rh-C} = 40 Hz, CO), 12.7 (J_{Rh-C} = 26 Hz, CH_2), 11.8 (CH_3). **8**: IR (cm^{-1}) 1642. ^1H NMR 0.68 (d, J_{Rh-H} = 2.2 Hz, 3 H, CH_3). ^{13}C NMR 233 (d, J_{Rh-C} = 39 Hz, CO), −2.2 (d, J_{Rh-C} = 25 Hz, CH_3). These complexes did not melt below 250 °C but merely darkened upon heating.

(20) Suggs, J. W.; Wovkulich, M. J.; Cox, S. D., manuscript in preparation.

to find any that fail to give carbon–carbon bond cleavage products.

Phosphines (such as PMe_3 or PPh_3) and CO cause facile ligand-promoted reductive elimination of **6–8** back to the starting ketones.[21] This fact explains why $RhCl(PPh_3)_3$ does not react with **1–3** and has obvious implications for the selection and design of other transition-metal reagents for carbon–carbon bond activation.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE-8207269) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society. The National Science Foundation contributed to the purchase of the Nicolet diffractometer.

Supplementary Material Available: Atom coordinates, temperature factors, and bond lengths and angles for compound **6** (5 pages). Ordering information is given on any current masthead page.

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[21] A mechanistic study of this ligand-promoted reductive elimination reaction shows, in the case of PPh_3, reductive elimination occurs from a five-coordinate complex in which pyridine is replaced by PPh_3.[20]

Photochemistry and Photophysics of Phenylmethyl Radicals†

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The photophysics of arylalkyl radicals, notably that of the prototype benzyl radical ($PhCH_2\cdot$), • have been extensively studied. Fluorescence lifetimes and quantum yields have been experimentally measured in solid matrices at low temperatures and theoretical calculations have estimated the energy levels and the various decay modes of a variety of substituted benzyl radicals.[1-7] Fluorescence from the closely related diphenylketyl radical has also been observed in a glassy matrix[8] as well as at room temperature.[9-11] For the ketyl radical the fluorescence lifetime has decreased from ~20 to ~2 ns on increasing the temperature from 77 K to room temperatue, indicating a possible photochemical reaction of the excited state of the radical at the higher temperature.[8] While the fluorescence lifetime of the benzyl and its analogue radicals at 77 K is in the range of 1.0 ± 0.5 μs, no information is available in the literature on their fluorescence lifetime at higher temperatures. In fact, information on the photochemistry and photophysics of radicals in liquid solutions is very scarce. To bridge this gap, we have initiated a systematic study of such systems. In the present communication we report on the room temperature lifetime, excited-state doublet–doublet and fluorescence spectra of the diphenylmethyl radical as well as on the photochemistry of its triphenylmethyl homologue.

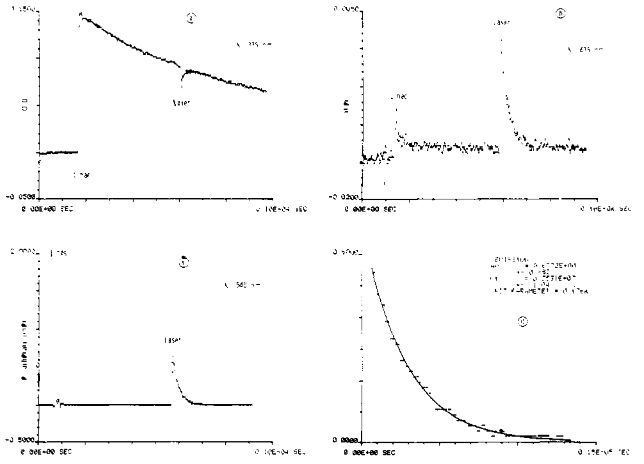

Figure 1. Excitation of diphenylmethyl radicals detected at different regions of the spectrum: (a) λ = 335 nm, bleaching of the ground state; (b) λ = 435 nm, doublet–doublet absorption by the excited state of the radical; (c) λ = 540 nm, fluorescence of the excited radical. Argon-saturated solution of 1 mM Ph_2CHCl in CH_3CN; (d) expansion of (c) to show least-squares best fit to exponential decay of the fluorescence.

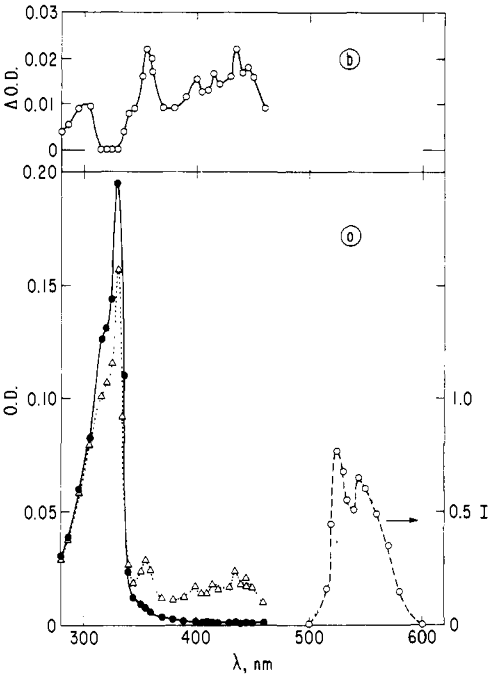

Figure 2. Fluorescence and absorption spectra of the $Ph_2CH\cdot$ radical; (a) absorption spectrum of the ground state before the laser flash (solid curve and solid points); absorption at the end of the laser flash (dotted curve and open triangles); fluorescence spectrum of the first excited doublet state (dashed line). (b) Doublet–doublet absorption spectrum of the first excited state of the radical; calculated assuming $\Delta OD = 0$ at 330 nm. Errors for ΔOD are <±10%. Spectra obtained following pulse radiolysis of 10^{-3} M Ph_2CHCl in CH_3CN.

The diphenylmethyl and triphenylmethyl radicals were produced pulse radiolytically by 40-ns electron pulses (~5 μM of radicals

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† Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Science, US-DOE under Contract W-31-109-ENG-38.

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