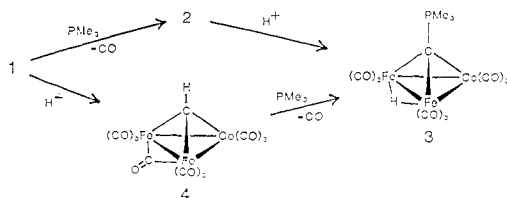


Figure 1. An ORTEP drawing of $[\text{Fe}_2\text{Co}(\text{CO})_9(\text{CPMe}_3)]^-$. Some selected bond distances (\AA): $\text{Co1-Fe2} = 2.5460$ (7), $\text{Co1-Fe3} = 2.5332$ (6), $\text{Fe2-Fe3} = 2.5567$ (8), $\text{Co1-C1} = 1.914$ (3), $\text{Fe2-C1} = 1.934$ (3), $\text{Fe3-C1} = 1.903$ (3), $\text{C1-P1} = 1.715$ (3), $\text{av P1-CH}_3 = 1.792$ (3).

Scheme I



face. The C1-P1 distance, 1.715 (3) \AA , is significantly shorter than the three equivalent P1-CH_3 distances (av 1.792 (3) \AA). In comparison to organic and organometallic phosphorus ylides,⁸ the C1-P1 distance is longer than the C=P bond of $\text{Ph}_3\text{P=CH}_2$ (1.661 (8) \AA)⁹ but shorter than or similar to the C=P bonds of phosphorus ylides bridging two metal centers ($1.750(18) - 1.82(4)$ \AA).¹⁰⁻¹³

Compound **2** does not react further with excess PMe_3 and cannot be reconverted to **1** under CO . Protonation of **2** using HSO_3CF_3 occurs across the Fe-Fe bond, giving $\text{HF}_2\text{Co}(\text{CO})_9(\text{CPMe}_3)$ (**3**).¹⁴ Compound **3** can also be generated from the reaction of $\text{Fe}_2\text{Co}(\text{CO})_{10}(\mu_3\text{-CH})$ (**4**)¹⁵ with PMe_3 , a reaction in which the phosphine induces C-H bond cleavage. The reaction of **4** with PMe_3 was monitored by ^1H , ^{13}C , and ^{31}P NMR spectroscopies and initially gave spectra which suggested the formation of numerous intermediates. Nonetheless, **3** is produced cleanly upon completion of the reaction. Scheme I summarizes the reactions described above.

Compound **1** can be viewed as a heteroatomic carbonyl cluster based on a pseudotetrahedral M_3C core. This treatment of **1** is in accordance with the valence formalisms of Wade¹⁶ and Mingos.¹⁷ In addition, an analogy is evident between eq 1 and ligand

substitution reactions of tetranuclear metal carbonyl clusters. Indeed, **1** and a four-metal analogue, $[\text{Fe}_4(\text{CO})_{13}]^{2-}$, exchange all CO ligands with ^{13}C gas at a comparable rate.^{5,18} Despite the ease with which **2** is formed, phosphine substitution for CO at the carbon vertex of $\text{M}_3(\text{CO})_9(\text{CCO})$ clusters is not a general reaction. The reaction of $[\text{Co}_3(\text{CO})_9(\text{CCO})]^+$ with PPh_3 leads to substitution at Co , yielding $[\text{Co}_3(\text{CO})_8(\text{PPh}_3)(\text{CCO})]^+$.¹⁹ Thus the relative affinities of carbonyl and phosphine ligands for carbon and metal centers appear to be delicately balanced in these clusters.

The reaction shown in eq 1 is surprisingly facile considering the evidence for a strong C=CO bond in **1** (C-CO distance = 1.29 (5) \AA ⁵ and $^1J_{\text{CC}} = 79.4$ Hz ¹⁵). The kinetic facility of this ligand displacement reaction at carbon may be the result of a transition state in which a ligand bridges between the metal framework and the capping carbon atom. A transition state of this type has been proposed in the synthesis of $\text{H}_2\text{Ru}_3(\text{CO})_9(\text{C-CO})$.²⁰ Evidence for incipient ligand bridging is evident in the structure of **1**, in which the CCO moiety tilts toward one Fe atom,²¹ thus forming a semibridging CO between the C and Fe atoms. Ligand bridging may also facilitate the previously cited exchange of the carbon-bound CO ligand of **1** with gaseous ^{13}C and to the displacement of the carbon-bound proton of **4** by PMe_3 (Scheme I). The tendency for the $\text{M}_3(\text{CO})_9$ ensemble to delocalize electron density from the capping carbon atom may also lower the energy of the transition state for ligand exchange.

Acknowledgment. This research was supported by the NSF Synthetic Inorganic-Organometallic Chemistry Program.

Supplementary Material Available: Tables of crystal data, positional parameters, anisotropic thermal parameters, and bond distances and angles for $[\text{PPN}][\text{Fe}_2\text{Co}(\text{CO})_9\text{CP}(\text{CH}_3)_3]$ (30 pages); tables of observed and calculated structure factors for $[\text{PPN}][\text{Fe}_2\text{Co}(\text{CO})_9\text{CP}(\text{CH}_3)_3]$ (41 pages). Ordering information is given on any current masthead page.

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Photochemistry of Aryl Azides: Detection and Characterization of a Dehydroazepine by Time-Resolved Infrared Spectroscopy and Flash Photolysis at Room Temperature

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The photochemistry of the aromatic azides (ArN_3) has been a subject of interest and some controversy for more than 60 years.³ Their irradiation leads to loss of nitrogen and to the formation of one or more reactive intermediates. For example, irradiation of phenyl azide creates its excited singlet state which loses nitrogen to give the singlet nitrene. Singlet phenylnitrene can intersystem cross to form its ground-state triplet which has been detected by ESR spectroscopy.⁴ Azobenzene is formed by dimerization of

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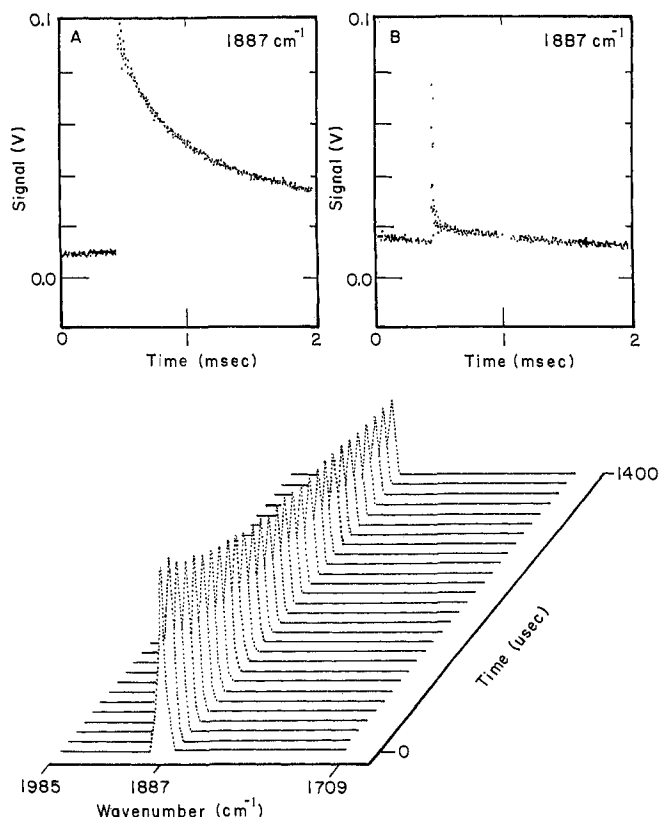
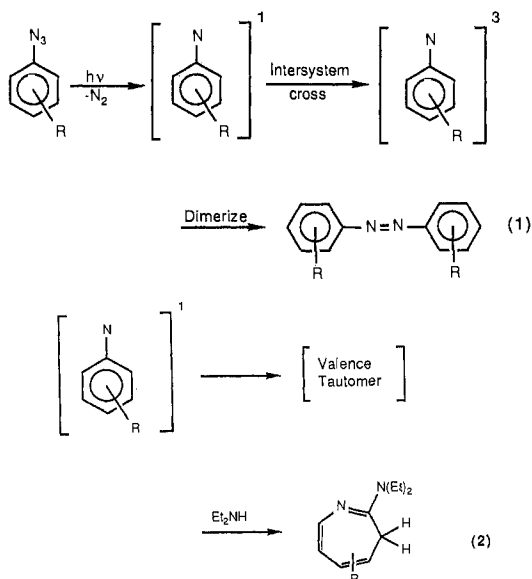


Figure 1. Photolysis of azide **1** in cyclohexane with time-resolved IR detection of the transient intermediate. Inset A shows the decay of the 1887-cm⁻¹ absorption assigned to dehydroazepine **3** in the absence of DEA; inset B, the decay of **3** in the presence of ca. 0.01 M DEA.

the triplet nitrene.⁵ Reversible isomerization of the singlet nitrene to a ground-state intermediate competes with formation and dimerization of the triplet nitrene.⁶ The valence isomer can be trapped by added nucleophiles (such as diethylamine, DEA) to give 2-substituted-3*H*-azepines⁷ which are often the major products of reaction under these conditions, eq 1 and 2.



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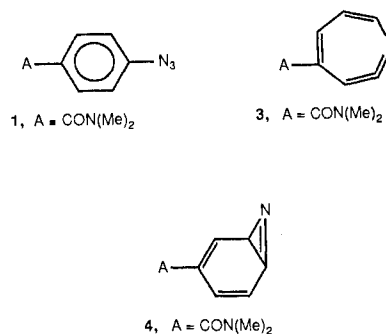
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The structure of the valence isomers formed from singlet nitrenes has been a matter of considerable interest. Huisgen and co-workers suggested first that they are bicyclic azirines.⁸ Later, Sunberg and co-workers,⁹ by analogy from the gas-phase work of Wentrup,¹⁰ proposed an alternative dehydroazepine structure. This suggestion was strengthened by Chapman and LeRoux¹¹ who recorded an infrared spectrum characteristic of the dehydroazepine by irradiating phenyl azide in an argon matrix at 8 K. However, Dunkin and co-workers¹² showed that azirines may be converted to dehydroazepines by irradiation, and it is widely recognized that detection of an intermediate isolated in a matrix at low temperature does not mean necessarily that the same species is present at higher temperature or that it participates under other reaction conditions. This is apparently true in this case since Platz, Wirz, and co-workers¹³ have recently shown that irradiation of phenyl azide at 77 K gives primarily the triplet nitrene.

We report herein investigation of the photochemistry of 4-(dimethylamido)phenyl azide (**1**)¹⁴ at room temperature in fluid



solution by transient absorption techniques with detection by infrared and ultraviolet spectroscopy. These experiments establish with certainty the intermediacy of 5-(dimethylamido)-1,2-dehydroazepine (**3**), identify it as the species trapped by nucleophiles, permit the estimation of its lifetime, and allow measurement of the rate of its reaction with DEA.

Irradiation of azide **1** at room temperature in deoxygenated cyclohexane solution (5×10^{-3} M, 350 nm, Rayonet Photoreactor) gives 4,4'-(dimethylamido)azobenzene in ca. 72% yield.¹⁵ When DEA (0.05 M) is present in the photolysis solution, 2-(diethylamino)-5-(dimethylamido)-3*H*-azepine (**2**)¹⁶ is isolated in nearly quantitative yield, eq 3. By analogy with phenyl azide, the 3*H*-azepine may be considered to arise from the reaction of either an intermediate dehydroazepine **3** or an azirine **4**. These two possibilities were distinguished by transient spectrophotometric techniques.

The most distinctive spectral features that allow differentiation of a dehydroazepine from an azirine occur in the IR region.^{11,12} Spectra of these intermediates isolated in matrices reveal a strong ketenimine absorption band for dehydroazepines at ca. 1890 cm⁻¹ and a characteristic band for azirines at ca. 1730 cm⁻¹. Time-

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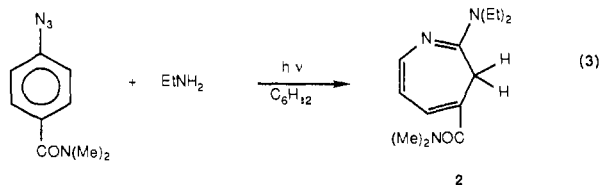
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(15) 4,4'-Bis(dimethylamido)azobenzene: ¹H NMR (CDCl₃) δ 3.1 (d, 12 H), 7.75–7.9 (d, 8 H). Anal. Calcd. for C₁₈H₂₀N₄O₂: C, 66.65; H, 6.21; N, 17.27. Found: C, 66.65; H, 6.22; N, 17.25.

(16) 2-(diethylamino)-5-(dimethylamido)-3*H*-azepine: ¹H NMR (CDCl₃) δ 1.25 (t, 6 H), 2.70 (d, 2 H), 2.80 (s, 3 H), 3.0 (s, 3 H), 4.15 (t, 4 H), 5.45 (t, 1 H), 6.1 (d, 1 H), 7.05 (d, 1 H); exact mass calcd for C₁₃H₂₁N₃O 235.1684, found 235.1694.



resolved IR spectra recorded following flash photolysis (308 nm, 100 mJ, 10 ns) of azide **1** in cyclohexane (2×10^{-3} M) at room temperature are shown in Figure 1. The region of the IR spectrum examined ($1709\text{--}1985\text{ cm}^{-1}$) is limited by the probing CO laser, and the time resolution of the experiment ($>1\ \mu\text{s}$) is set by the response of the detector.¹⁷

The time-resolved IR spectra of the intermediate formed by photolysis of **1** shows a single, strong absorption band at 1887 cm^{-1} , clearly identifying it as dehydroazepine **3**. There are no detectable absorptions characteristic of azirine **4** in the examined spectral region. The dehydroazepine is formed within the rise time of the laser apparatus and decays following an approximate first-order rate law (inset A on Figure 1) with an initial half-life of ca. 1 ms. Further confirmation of the structure of the intermediate comes from verification of its rapid reaction with amines. Irradiation of **1** in cyclohexane solution containing ca. 0.01 M DEA also gives the 1887-cm^{-1} band of the dehydroazepine, but under these conditions it decays away in a few μs (inset B on Figure 1). The rate of reaction of the dehydroazepine with DEA can be measured more accurately by flash photolysis with UV spectral detection.

Irradiation of azide **1** (2×10^{-4} M) in deoxygenated cyclohexane with a quadrupled Nd-YAG laser (266 nm, 4 mJ, 20 ns) generates an intermediate whose UV absorption spectrum recorded $2\ \mu\text{s}$ after the laser pulse is shown in Figure 2A. This species is formed immediately on the time scale of this experiment (ca. 20 ns) and then decays with a half-life of ca. 1 ms, Figure 2B. When DEA is present in solution, a new, strong absorption band with maximum at ca. 365 nm (Figure 2C) grows into the spectrum with a rate that is directly proportional to the amine concentration. Analysis of these results yields a second-order rate constant for the reaction of DEA with the intermediate of $4.4 (\pm 0.5) \times 10^7\ \text{M}^{-1}\ \text{s}^{-1}$, Figure 2D.

It is normally a difficult matter to assign with certainty the structure of a transient intermediate detected solely by UV spectroscopy. In the present case however, IR and UV spectral detection in combination with the kinetic measurements leads to sensible assignment of the spectrum shown in Figure 2A to dehydroazepine **3**. The product formed directly from the reaction of DEA with **3** does not have any IR absorptions in the region probed. However, its UV spectrum (Figure 2D) and the isolation of 3*H*-azepine **2** in high yield support Sundberg's suggestion that the detected species is the 1*H*-azepine precursor to **2** formed by addition of DEA across the carbon-nitrogen double bond of **3**.¹⁸

These experiments resolve the long-standing debate concerning the structure of the intermediates formed by irradiation of phenyl azides at room temperature. Ring expansion to the dehydroazepine is the exclusive fate for azide **1**. The dehydroazepine has a lifetime of ca. 1 ms in the absence of a nucleophilic trapping reagent and may isomerize with moderate efficiency to the triplet nitrene (presumably first passing through the singlet). There is no evidence for the existence or participation of azirine **4** in these reactions.¹⁹ Comparison of these results with product, kinetic, and spectral data for phenyl azide itself shows excellent correspondence.⁵ On this basis we conclude that ring expansion to the dehydroazepine is also the dominant pathway in the irradiation of phenyl azide. This finding will necessitate careful reevaluation

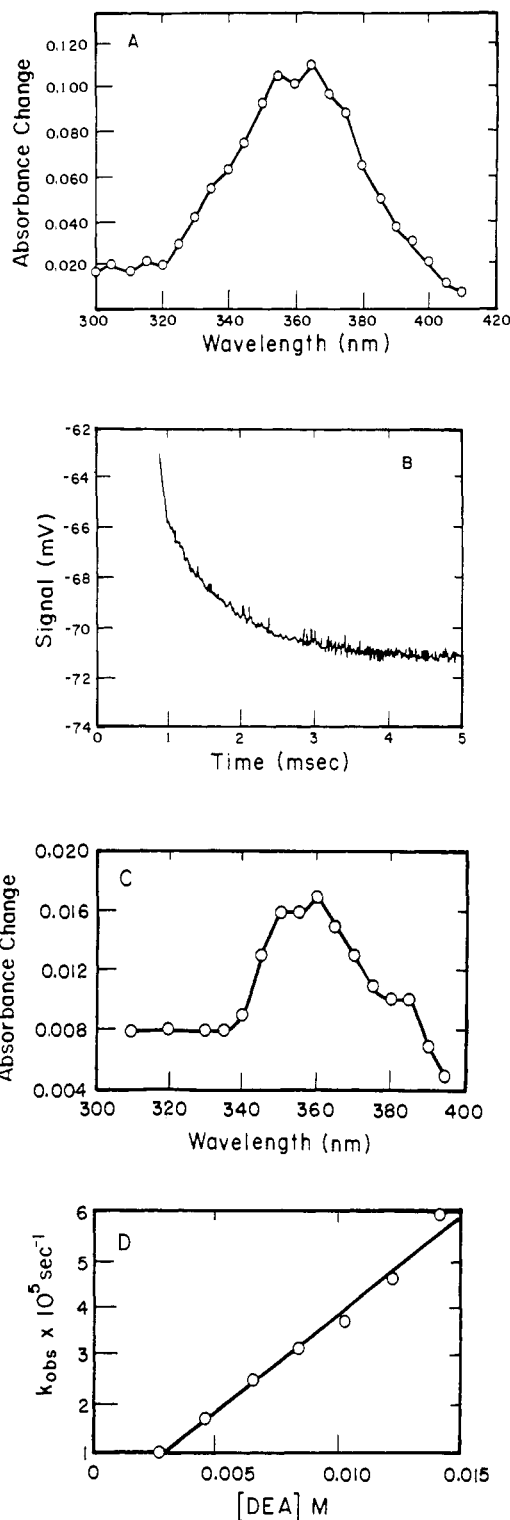


Figure 2. Flash photolysis of azide **1** in cyclohexane with UV detection of the transient intermediate. Part A shows the spectrum recorded $2\ \mu\text{s}$ after the laser flash in the absence of DEA; part B shows the decay of the absorption assigned to dehydroazepine **3** monitored at 360 nm; part C shows the spectrum recorded $100\ \mu\text{s}$ after the flash in the presence of 0.015 M DEA; part D is a plot of the pseudo-first-order rate constant (k_{obs}) for reaction of **3** with DEA.

of the hypothetical "molecular explosion in solution" of phenyl azide which was supported in part by improper assignment of the dehydroazepine absorption spectrum to triplet phenylnitrene.²⁰

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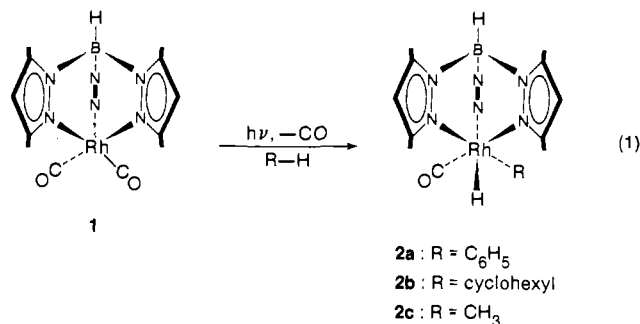
Efficient and Selective Carbon-Hydrogen Activation by a Tris(pyrazolyl)borate Rhodium Complex

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Pyrazolylborate-transition-metal chemistry has developed extensively over 20 years¹ but has not previously intersected the area of carbon-hydrogen activation. We now report that the tris(dimethylpyrazolyl)borato complex (HBPz*₃)Rh(CO)₂ (**1**, Pz* = 3,5-dimethylpyrazolyl)² photochemically activates aromatic and



saturated hydrocarbons with great efficiency and high thermodynamic selectivity at room temperature. Unlike previously reported photochemical systems, activation proceeds under daylight or tungsten illumination as well as with use of a mercury arc.

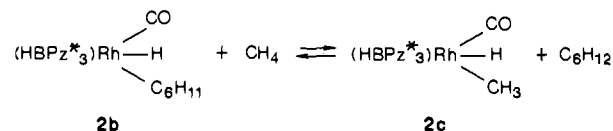
When a pale yellow solution of **1** (ca. 2 mM) in a closed, evacuated Pyrex Schlenk tube was irradiated under standard conditions³ for 5 min by means of a 450-W Hanovia medium pressure mercury lamp, the solution became colorless, and conversion to the hydridophenyl rhodium(III) complex **2a** according to eq 1 was complete. Under the same conditions, conversion of (η⁵-C₅Me₅)Ir(CO)₂ to the hydridophenyl complex was only ca. 60% after 6-h irradiation, and there was general degradation at longer times.³ Activations using (η⁵-C₅Me₅)Ir(PMe₃)H₂ also require long irradiation with a powerful UV source and do not proceed to completion.⁴ After 2-h irradiation at a distance of 2-3 cm from an ordinary 75-W incandescent reflector flood light, a benzene solution of **1** (2.9 mM) was >95% converted to **2a**.

Complex **2a** is a moderately air stable colorless crystalline solid, although crystals of X-ray quality have not yet been obtained. The six methyl resonances in the ¹H NMR spectrum are consistent with the three nonequivalent pyrazole rings in the octahedral structure; phenyl protons are broad at ambient temperature but sharpen at -20 °C to show five sharp sets of multiplets as rotation about the rhodium-phenyl bond slows. Above room temperature solutions of **2a** in benzene-*d*₆ undergo exchange forming (HBPz*₃)Rh(CO)(D)(C₆D₅) (t_{1/2} = 1.5 h at 60 °C) at a rate similar to that observed for (η⁵-C₅Me₅)Rh(PMe₃)(H)(C₆H₅).⁵

Irradiation of **1** (ca. 1.8 mM) at room temperature in rigorously purified cyclohexane⁶ in an evacuated vessel resulted in partial conversion to the cyclohexyl hydride **2b** (ν_{CO} 2028 cm⁻¹ in cyclohexane). Infrared spectra showed complete conversion of **1** to **2b** within 5 min when a N₂ or Ar purge was used during photolysis to prevent the back reaction with released CO. In view of its lability and limited stability,⁷ **2b** was not isolated but converted with minimum delay by reaction with CCl₄ to the chloro derivative (HBPz*₃)Rh(CO)(Cl)(C₆H₁₁) (**3**) for full characterization.⁸

Addition of a slight excess of benzene to a freshly prepared cyclohexane solution of **2b** at 25 °C results in its quantitative conversion to **2a** within 10 min. This transformation underlines the lability of **2b** and relative stabilities in the system;⁹ **2b** is a remarkably efficient scavenger for aromatic hydrocarbons.

A fresh cyclohexane solution of **2b** (2.2 mM) was prepared with N₂ as purge. The lamp was extinguished, and the purge was changed to CH₄. After 17 min, the solution exhibited IR bands at 2035 cm⁻¹ (assigned to (HBPz*₃)Rh(CO)(H)(CH₃), **2c**), 2028 cm⁻¹ (**2b**), and weak bands of decomposition products.⁷ The ratio of absorbances of the 2035- and 2028-cm⁻¹ bands was ca. 0.6.¹⁰ Another estimate of the molar ratio **2c**:**2b** was 0.63, obtained from the ¹H NMR of the mixture of stable chloride derivatives (HBPz*₃)Rh(CO)(Cl)(CH₃) (**4**) and **3** resulting from reaction with excess CCl₄. At 25 °C, the solubility of CH₄ is 0.0302 M,¹¹ [cyclohexane] is 9.20 M, and whence K_{eq} ≈ 190 for eq 2. This indicates a reasonably high equilibrium selectivity favoring the primary rhodium-methyl bond and its minimal (though not negligible) steric requirement.¹²



As judged from carbonyl-stretching frequencies, the electron richness of **1** (ν_{CO} 2054, 1981 cm⁻¹ in hexane) is similar to that of (η⁵-C₅H₅)Rh(CO)₂ (ν_{CO} 2049, 1986 cm⁻¹ in hexane); the averages of the band pairs are identical. The ability of **1** to function with near UV light presumably results from the position of its lowest energy electronic absorption band at 353 nm.¹⁵ High quantum efficiency is also necessary for response to the much less intense incandescent and daylight sources. Although the origin of this efficiency is not yet clear, we speculate that it may involve facile tridentate-bidentate interconversions of the tris(pyrazolyl)borate ligand. It is hoped that experiments in collaboration with Dr. A. J. Rest (University of Southampton) involving **1** in Nujol mulls at 12 K will clarify the primary photoprocess.

On the basis of the foregoing results, we are expanding our investigation of pyrazolylborate complexes and their interaction with hydrocarbons, with rhodium and iridium the current focus. It is now clear that there are the expected similarities¹ to C₅H₅ and C₅Me₅ systems, while preliminary results suggest some

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(7) Monitoring the cyclohexane solution by IR shows the disappearance of **2b** within 2-3 h in the dark at room temperature as new, weaker bands appear at 2048 and 2040 cm⁻¹. This process is under investigation.

(8) Reaction with CCl₄ was fast, and yields of isolated **3** after chromatographic purification were 70-75%.

(9) Displacement of alkane by arene in (η⁵-C₅Me₅)M(PMe₃)(H)(R) complexes appears general. Rates are significant at -17 °C for M = Rh⁵ but only above 100 °C for M = Ir.^{4c}

(10) Absolute yields of **2c** and **2b** were not accurately determined but were estimated from IR band intensities to account for >90% of **1** used in the reaction.

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(12) With the assumption that ΔS° = 0 in eq 2, ΔH° ≈ -3 kcal. By using established values of D(H-CH₃) and D(H-C₆H₁₁),¹³ one estimates {D(Rh-CH₃) - D(Rh-C₆H₁₁)} = 13 kcal/mol at 25 °C, a further indication of the variability of D(M-R) with the organic group.^{4c,5,14}

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(15) UV (solvent, λ_{max}, nm, ε). (HBPz*₃)Rh(CO)₂ (1): *n*-hexane, 221 (17600), 353 (1820). (η⁵-C₅Me₅)Ir(CO)₂: *n*-hexane, 220 (13000), 290 (5500). (η⁵-C₅Me₅)Ir(PMe₃)H₂:^{4b} cyclohexane, 259 (1600).

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