The reaction of $(OC)_3Mn^-$ with NH_3 is unique among the neutrals in Table I in that a CO ligand is *not* displaced from the adduct and we observe no kinetic isotope effect ($k_{NH_3}/k_{ND_3} = 1.0$). These facts lead us to conclude that the product is the simple adduct negative ion with NH_3 (or ND_3) occupying a metal coordination site (eq 3). This structural conclusion is supported

$$\underset{m/z\ 139}{(OC)_3Mn^-} + NH_3 \xrightarrow{He} \underset{m/z\ 156}{(OC)_3Mn(NH_3)^-} \qquad (3)$$

by the results of ion–molecule reactions of adduct *m/z* 156 where the NH_3 (or ND_3) molecule is replaced intact in its reactions with H_2O and CH_3OH. This result is interesting since it will allow for a direct comparison of the kinetics and product branching fractions as a function of the presence vs. absence of a single coordinated "solvent" molecule. The fact that $(OC)_2Fe^{-}\cdot$ inserts into the N–H bond of NH_3, but $(OC)_3Mn^-$ does not, requires that the net bonding energy produced in the former insertion reaction exceeds that which would result by insertion with the Mn species.

The above neutral molecules are the simplest members of a number of organic functional group series which are presently being investigated. These results, and those with the group IV (group 14)[15] hydrides, will be reported in due course.

Acknowledgment. We thank the National Science Foundation for support of this research and Professor D. W. Setser for the samples of D_2S and ND_3 used and helpful discussions.

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(15) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

Rhenium Dinitrogen Complex (η-C_5Me_5)Re(CO)(PMe_3)(N_2). Facile Photochemical Generation of a Rhenium Intermediate and Oxidative Addition of Hydrocarbon C–H Bonds

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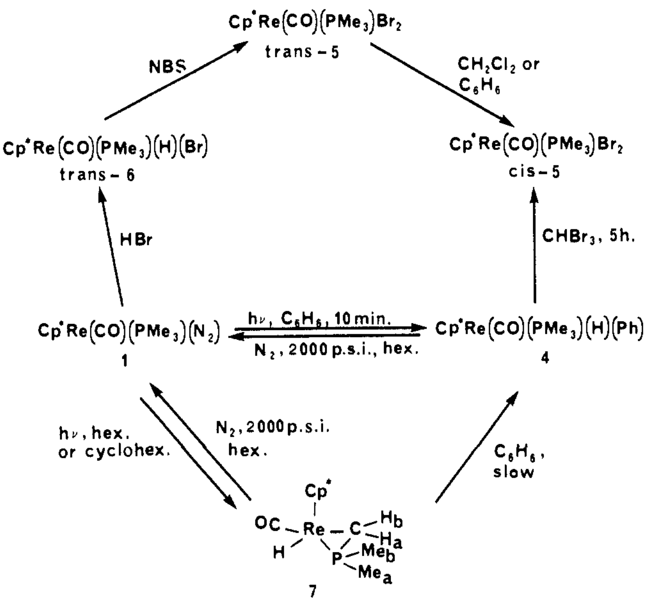
As part of our continuing investigation of dinitrogen, diazenide, hydrazide, and related ligands, we have synthesized the trimethylphosphine-substituted (pentamethylcyclopentadienyl)rhenium dinitrogen complex $Cp^*Re(CO)(PMe_3)(N_2)$ (**1**)[1] ($Cp^* = \eta$-C_5Me_5). The MeCN complex $[Cp^*Re(CO)(MeCN)(p$-$N_2C_6H_4OMe)][BF_4]$ (**2**)[2] was treated with PMe_3 to give $[Cp^*Re(CO)(PMe_3)(p$-$N_2C_6H_4OMe)][BF_4]$ (**3**), which was converted to **1** by using *t*-BuLi. Complex **1** is a pale yellow solid that is stable indefinitely if air is excluded and is inert to thermal exchange of the N_2 ligand in N_2-saturated organic solvents at ambient temperature as judged from the IR and ^{15}N NMR spectra of 96% $^{15}N_\alpha$-enriched samples. Nevertheless, **1** undergoes photochemical reactions in which the N_2 ligand is readily displaced. Most interesting and topical, in view of the current interest in C–H activation by soluble transition-metal complexes,[3,4] is the concurrent formation of a rhenium intermediate capable of insertion into selected hydrocarbon C–H bonds in high yield to give isolable derivatives. Bergman and co-workers[5] have recently published the first examples of the reaction of hydrocarbon C–H bonds with rhenium intermediates photogenerated from inter alia $Cp^*Re(CO)_2(PMe_3)$. Our results with the N_2 complex **1** are generally in agreement with and extend those of Bergman and likewise point to the involvement of the same, formally unsaturated, putative intermediate "$Cp^*Re(CO)(PMe_3)$" in the photolytic reactions.[6] Some results are summarized in Scheme I.

Scheme I



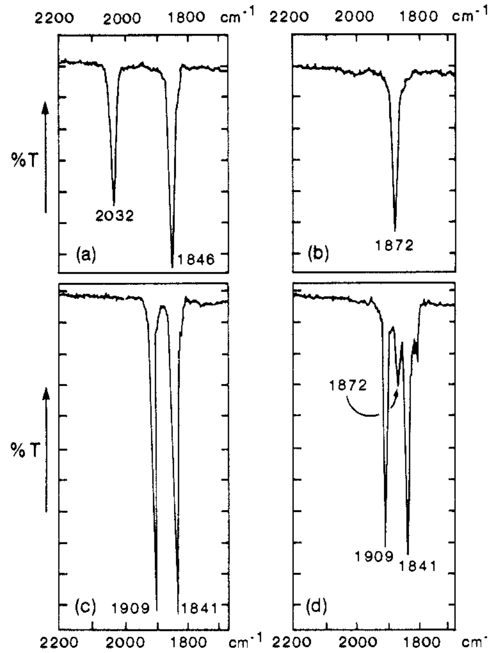


Figure 1. Comparison of the production of **4** [ν(CO) 1872 cm^{-1}] from the irradiation of $Cp^*Re(CO)(PMe_3)(N_2)$ (**1**) or $Cp^*Re(CO)_2(PMe_3)$ in benzene. IR spectra of (a) **1**, (b) 10-min irradiation of **1**, (c) $Cp^*Re(CO)_2(PMe_3)$, and (d) 10-min irradiation of $Cp^*Re(CO)_2(PMe_3)$.

Irradiation of **1** in benzene solution (Figure 1a) at room temperature for only 10 min (200-W Hanovia high-pressure lamp, quartz vessel, N_2 purge) resulted in quantitative conversion to a single carbonyl-containing product (Figure 1b), isolated from

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(1) For the parent dicarbonyl complex $Cp^*Re(CO)_2(N_2)$, see: Einstein, F. W. B.; Klahn-Oliva, A. H.; Sutton, D.; Tyers, K. G. *Organometallics* **1986**, *5*, 54.

(2) Barrientos-Penna, C. F.; Gilchrist, A. B.; Klahn-Oliva, A. H.; Hanlan, A. J. L.; Sutton, D. *Organometallics* **1985**, *4*, 478.

(3) Muetterties, E. L. *Chem. Soc. Rev.* **1983**, *12*, 283.

(4) For recent references, see: (a) Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 7190. (b) Wax, M. J.; Stryker, J. M.; Buchanan, J. M.; Kovac, C. A.; Bergman, R. G. *Ibid.* **1984**, *106*, 1121. (c) Jones, W. D.; Maguire, J. A. *Organometallics* **1986**, *5*, 590.

(5) Bergman, R. G.; Seidler, P. F.; Wenzel, T. T. *J. Am. Chem. Soc.* **1985**, *107*, 4358.

(6) Previous examples of photodissociation of N_2 from rhenium dinitrogen complexes in the presence of aromatic solvents have not resulted in isolable C–H activation products. See: (a) Bradley, M. G.; Roberts, D. A.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 379. (b) Hughes, D. L.; Pombeiro, A. J. L.; Pickett, C. J.; Richards, R. L. *J. Organomet. Chem.* **1983**, *248*, C26.

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hexane at −78 °C as a white solid and characterized by spectroscopy and analysis as the benzene C–H activation product *trans*-$Cp^*Re(CO)(PMe_3)(H)(Ph)$ (**4**). By way of comparison, we observed (Figure 1c,d) that irradiation of $Cp^*Re(CO)_2(PMe_3)$[5] under identical conditions gave only a low yield of **4**. The assignment of mutually trans H and C_6H_5 groups in **4** is based on the following results. The $^2J_{PH}$ value for the hydride resonance (66.7 Hz) indicates cis hydride and PMe_3 groups; the CO resonance has J_{CH} = 10.8 Hz and no observable coupling to P, indicating CO to be cis to the hydride and trans to PMe_3.[7] Furthermore, a strong NOE enhancement of the hydride and phenyl resonances resulted from irradiation of the PMe_3 proton signal. Additional confirmation comes from a comparison with the NMR spectra of the new compounds *cis*- and *trans*-$Cp^*Re(CO)(PMe_3)Br_2$ (**5**) and *trans*(H,Br)-$Cp^*Re(CO)(PMe_3)(H)(Br)$ (**6**) that have been synthesized in thermal reactions of **1**. The CO resonance in *cis*-**5** is coupled to the cis phosphorus atom with $^2J_{PC}$ = 24.9 Hz, whereas the CO resonance in *trans*-**5** is coupled to the trans phosphorus atom by only 3.7 Hz. Likewise, **6** is assigned a structure with trans CO and PMe_3 groups because $^2J_{PC}$ is too small to observe in the CO resonance, and it also has *cis*-PMe_3 and hydride groups from the value of $^2J_{PH}$ (55.7 Hz) for the hydride resonance (and the observation of a very strong NOE enhancement of this resonance on irradiating the PMe_3 protons).

Photolysis of **1** in hexane or cyclohexane for 10 min resulted in the complete disappearance of the dinitrogen complex and the formation of a single carbonyl product with a very strong, sharp ν(CO) at 1878 cm^{-1}. This was isolated at −78 °C as a white solid and characterized as the cyclometalated compound $Cp^*Re(CO)(\eta^2\text{-}PMe_2CH_2)(H)$ (**7**) resulting from intramolecular C–H activation of a methyl group of the PMe_3 ligand. The stereochemistry, in which the hydride is trans to the methylene carbon and cis to P, is assigned from NMR couplings and NOE results. The latter allows an unambiguous assignment of the inequivalent PMe and CH resonances. Compound **7** reacts slowly with benzene in the dark to form the hydridophenyl **4**. This suggests that reversible formation of "$Cp^*Re(CO)PMe_3$" from **7** occurs[5] and that **4** results from the thermal reaction of this intermediate with benzene. Consistent with this, when benzene-d_6 was employed the hydride resonance was totally absent in the NMR spectrum, proving that the product is exclusively $Cp^*Re(CO)(PMe_3)(D)(C_6D_5)$ and that the hydride of **7** is reincorporated wholly into the PMe_3 group of **4**, with the hydride of **4** arising wholly from the benzene solvent.

The reversible formation of "$Cp^*Re(CO)(PMe_3)$" from **7** is further indicated by the quantitative regeneration of the dinitrogen complex **1** when **7** is pressurized with N_2. More surprising is the observation that **1** is also formed essentially quantitatively (but more slowly) in hexane from the hydridophenyl complex **4** and N_2. This may indicate that, in solution **4** is partly dissociated into benzene and "$Cp^*Re(CO)(PMe_3)$" possibly via a benzene π-complex intermediate.[8] In agreement, the NMR and MS of **4** indicated about 20% conversion to $Cp^*Re(CO)(PMe_3)(D)(C_6D_5)$ in C_6D_6 at 8 °C over 6 days.

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Supplementary Material Available: Synthetic, spectral, and analytical data for compounds **1** and **3–7** (4 pages). Ordering information is given on any current masthead page.

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[7] For related stereochemical dependence of J_{PC} and J_{PH} in cis and trans piano stool carbonyl phosphine compounds, see: (a) Todd, L. J.; Wilkinson, J. R.; Hickey, J. P.; Beach, D. L.; Barnett, K. W. *J. Organomet. Chem.* **1978**, *154*, 151. (b) Pyshnograyeva, N. I.; Setkina, V. N.; Panosyan, G. A.; Petrovskii, P. V.; Makarov, Yu. V.; Kolobova, N. E.; Kursanov, D. N. *Ibid.* **1976**, *108*, 85. (c) Faller, J. W.; Anderson, A. S. *J. Am. Chem. Soc.* **1970**, *92*, 5852.

[8] Benzene complexes of $Cp^*Re(CO)_3$ have recently been identified: Van der Heijden, H.; Orpen, A. G.; Pasman, P. *J. Chem. Soc., Chem. Commun.* **1985**, 1576.

Charge-Transfer Sensitization of the Valence Photoisomerization of Norbornadiene to Quadricyclene by an Orthometalated Transition-Metal Complex

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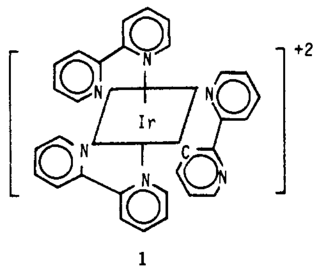
Some time ago we reported[1] that the orthometalated complex (2,2′-bipyrid-3-yl-C^3,N')bis(2,2′-bipyridine-N,N')iridium(III) (**1**)



1

sensitizes the valence photoisomerization of norbornadiene (**2**) to quadricyclene (**3**) with high quantum efficiency (eq 1). This

2, R = H
4, R = CO_2CH_3

3, R = H
5, R = CO_2CH_3

(1)

result was surprising on energetic grounds in that the lowest electronic excited state of **1** lies well below the reactive triplet state of the diene. Consequently, we have undertaken a more detailed investigation of the **1–2** system with the aim of delineating the key sensitizer–substrate interaction(s). Presented here are several lines of evidence that support a novel mechanism based upon photoinduced charge transfer.

Excitation of **1**[2] with 366-nm light produces a green luminescence[3] (λ_{max} 462, 491 nm) having a lifetime of 10.2 μs[4] in freshly purified acetonitrile at 25 °C. Addition of **2** strongly quenches this emission with no discernible alteration in band shape. Lifetime quenching data obey Stern–Volmer kinetics and yield a value of $1.4 \times 10^8\ M^{-1}\ s^{-1}$ for k_q, the bimolecular quenching rate constant. The quantum efficiency (ϕ_{isom}) for sensitized isomerization of **2** to **3** upon 366-nm irradiation in N_2-bubbled CH_3CN at 25 °C varies with both the diene concentration and the length of photolysis.[5] Measurements of ϕ_{isom} at short irradiation times were used to construct a linear plot of $1/\phi_{isom}$ vs. $1/[\mathbf{2}]$, from which values of $1.4 \times 10^8\ M^{-1}\ s^{-1}$ for k_q and 0.72 ± 0.05 for the limiting sensitization efficiency were obtained. The excellent agreement between the quenching rate constants calculated from lifetime and photochemical data argues strongly that the emissive excited state of **1** sensitizes the valence isomerization of **2**.

The photobehavior of the **1–2** system can be analyzed in terms of the general mechanism outlined in eq 2, where an asterisk

$$\begin{aligned} \mathbf{1}^* + \mathbf{2} \rightleftarrows [\mathbf{1}^*,\mathbf{2}] &\xrightarrow{\text{i}} \mathbf{1} + {}^3\mathbf{2} \rightarrow \mathbf{1} + \mathbf{2} \text{ or } \mathbf{1} + \mathbf{3} \\ &\xrightarrow{\text{ii}} X \rightarrow \mathbf{1} + \mathbf{2} \text{ or } \mathbf{1} + \mathbf{3} \end{aligned} \qquad (2)$$

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[1] Kutal, C. *Adv. Chem. Ser.* **1978**, *168*, 158.

[2] Synthesis: Kahl, J. L.; Hanck, K.; DeArmond, K. *J. Inorg. Nucl. Chem.* **1979**, *41*, 495.

[3] (a) This luminescence originates from an excited state containing contributions from intraligand and metal-to-ligand charge-transfer configurations.[3b–d] (b) Watts, R. J.; Harrington, J. S.; Van Houten, J. *J. Am. Chem. Soc.* **1977**, *99*, 2179. (c) Braterman, P. S.; Heath, G. A.; MacKenzie, A. J.; Noble, B. C.; Peacock, R. D.; Yellowlees, L. J. *Inorg. Chem.* **1984**, *23*, 3425. (d) Finlayson, M. F.; Ford, P. C.; Watts, R. J. *J. Phys. Chem.*, in press.

[4] Because of self-quenching, the luminescent lifetime of **1** varies with concentration. Lifetime values measured in CH_3CN at 25 °C are as follows: 10.2 μs (1×10^{-6} M), 10.2 μs (1×10^{-5} M), 0.1 μs (4×10^{-4} M).

[5] Competitive quenching by **3** (vide infra) formed photochemically lowers ϕ_{isom} at longer irradiation times.

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