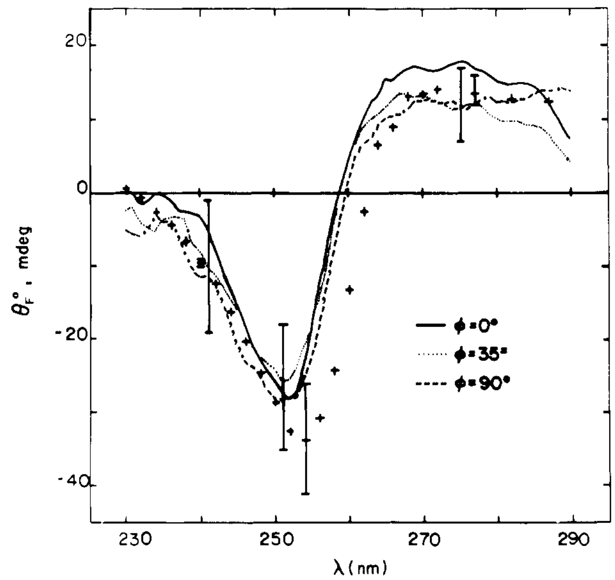

Figure 1. Photoselected FDCD spectra of 2.5×10^{-4} M morphine in 90:10 glycerol-water (v/v), 0.1 N H_2SO_4: (—) $\phi = 0°$; (···) $\phi = 35°$; (- - -) $\phi = 90°$; (+) spectrum predicted from CD and absorption data. Filter was Wratten 18-A. A cylindrical CD sample cell with 10-mm pathlength was used. Baselines were obtained by turning off the excitation modulator. Data were taken with a PDP 11/34 minicomputer; five scans each of the spectrum and baseline were averaged.

However, the average of spectra measured for $\phi = \pm 35°$ by using two phototubes agrees well with the spectrum predicted from CD and absorption measurements.[3,7] Any residual discrepancy is probably due to noise and practical problems in making the calculation. Thus the error bars for the calculated points represent the effects of 0.5-nm errors in wavelength calibration of the spectrometers.[13] Spectra for $\phi = 0°$ and 90° are also shown in Figure 1. Within experimental error, they are the same as the 35° spectrum. This implies the optical activity for excitation with k vector along the emission transition moment is similar to the average optical activity.[8]

A second potential problem for FDCD is suggested by the work of Tran and Fendler.[6,14] They report the quantum yield for L-tryptophan fluorescence differs by about 10% between excitation by LCPL and RCPL. A similar effect is observed with D-tryptophan. All current theories of FDCD assume this difference is negligible, so the measurement reflects only the difference in *absorption* for LCPL and RCPL. The disagreement is serious since current theories predict an FDCD signal of about −5 mdeg for L-tryptophan, whereas the effect described by Tran and Fendler would result in a signal of +1600 mdeg. They also point out that no FDCD spectra have been measured for enantiomers. To fill this gap, we report in Figure 2 the FDCD spectra of D- and L-tryptophan in water,[15] along with spectra predicted from CD and absorption measurements.[3] The excellent agreement and small magnitude indicate the results of Tran and Fendler are in error. We cannot rationalize this discrepancy.

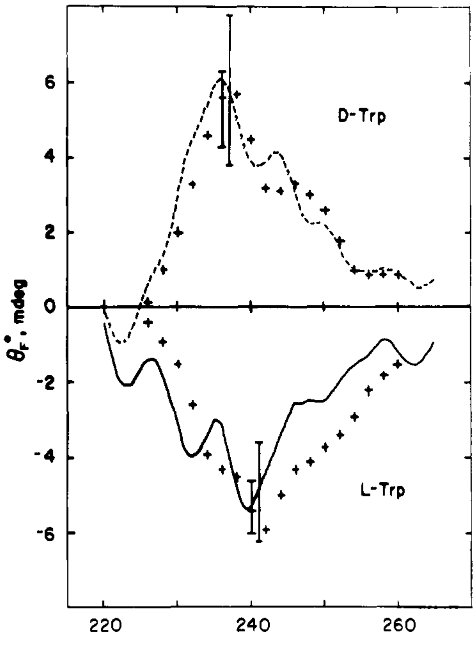

Figure 2. FDCD spectra of 5×10^{-5} M D-, L-tryptophan in water, 25 mM Na_2HPO_4, pH 10.9: (- - -), D-tryptophan; (—) L-tryptophan; (+) spectrum predicted from CD and absorption data. No polarizer was used since the fluorescence is isotropic. Baseline was 5×10^{-5} M DL-tryptophan. DL-Tryptophan and indole baselines were coincident. See Figure 1 for other conditions.

The results reported here indicate the quantum yield for fluorescence is independent of the circular polarization of excitation. Therefore FDCD spectra can be related directly to transmission CD. The morphine spectra were measured for a polarization ratio and signal size similar to that expected for proteins. The good agreement with theory indicates it is now possible to measure FDCD spectra of tryptophan in proteins and interpret them much like conventional CD spectra.

Acknowledgment. We thank Dr. Werner Hug for kindly sharing his results with us and for several stimulating discussions. We also thank W. C. Schaefer for his invaluable assistance in designing and building the electronics. Funding from the Research Corporation was essential for initiating this work. E.W.L. is an N.I.H. predoctoral trainee (Grant ST32GM07230) and the work was supported by N.I.H. Grant GM22939.

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[12] The linear depolarization ratio is defined and measured according to Parker. (C. A. Parker, "Photoluminescence of Solutions"; Elsevier, New York, 1968; pp 53, 301.)

[13] Holmium oxide glass is used to check the wavelength calibration of the absorption and CD instruments. Because the FDCD calculation is very sensitive to this wavelength calibration, the FDCD instrument is calibrated more directly. A cell containing d-10-camphorsulfonic acid (CSA) is placed in the excitation beam ahead of the sample cell. The sample cell is filled with optically inactive sodium fluorescein. The sodium fluorescein fluorescence is a *direct* measure of the CSA transmission CD, which is accurately known.

[14] Tran, C. D.; Fendler, J. H. In "Origins of Optical Activity in Nature", D. C. Walker, Ed.; Elsevier, Amsterdam, 1979; Chapter 5.

[15] CD and FDCD spectra for D- and L-tryptophan in methanol, the solvent used by Tran and Fendler, were too small to measure accurately.

[16] Alfred P. Sloan Fellow.

Cationic Alkylidyne–Trirhodium Cluster Complexes. Crystal Structure of $[(\eta^5\text{-}C_5H_5)_3Rh_3(\mu\text{-}CO)_2(\mu_3\text{-}CH)]PF_6$

Sir:

In recent years a number of transition-metal compounds with bridging methylene groups (μ-CH_2) have been synthesized and characterized.[1,2] Currently, attention is focused on examining

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[1] (a) $(\eta^5\text{-}C_5H_5)_2Mn_2(CO)_4(CH_2)$: Herrmann, W. A.; Reiter, B.; Biersack, H. *J. Organomet. Chem.* **1975**, *97*, 245. (b) $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_2(CH_2)$: Herrmann, W. A.; Kruger, C.; Goddard, R.; Bernal, I. *Ibid.* **1977**, *140*, 73. (c) $Pt_2Cl_2(Ph_2PCH_2PPh_2)_2(CH_2)$: Brown, M. P.; Fisher, J. R.; Franklin, S. J.; Puddephatt, R. J.; Seddon, K. R. *J. Chem. Soc., Chem. Commun.* **1978**, 749. (d) $H_2Os_3(CO)_{10}(CH_2)$: Schultz, A. J.; Williams, J. M.; Calvert, R. B.; Shapley, J. R.; Stucky, G. D. *Inorg. Chem.* **1979**, *18*, 319. (e) $Ru_2(PMe_3)_6(CH_2)_3$: Hursthouse, M. B.; Jones, R. A.; Malik, K. M. A.; Wilkinson, G. *J. Am. Chem. Soc.* **1979**, *101*, 4128. (f) $(\eta^5\text{-}C_5H_4CH_3)_2Mn_2(CO)_4(CH_2)$: Creswick, M.; Bernal, I.; Herrmann, W. A. *J. Organomet. Chem.* **1979**, *172*, C39. (g) $Fe_2(CO)_8(CH_2)$: Sumner, C. E., Jr.; Riley, P. E.; Davis, R. E.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 1752.

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Table I. Selected Bond Lengths (Å) and Bond Angles (Deg) for $[(\eta^5\text{-}C_5H_5)_3Rh_3(\mu\text{-}CO)_2(\mu_3\text{-}CH)]PF_6$

Bond Lengths			
Rh(1)–Rh(2)	2.6889 (4)	Rh(2′)–C(10)	1.918 (5)
Rh(2)–Rh(2′)	2.6815 (4)	Rh(1)–C(9)	1.944 (5)
Rh(1)–C(10)	2.267 (5)	Rh(2)–C(9)	1.980 (4)
Bond Angles			
Rh(1)–C(10)–O(11)	127.2 (4)	Rh(2)–C(9)–Rh(2′)	85.2 (2)
Rh(2)–C(10)–O(11)	153.2 (4)	Rh(1)–C(9)–H(9)	131 (4)
Rh(1)–C(9)–Rh(2)	86.5 (2)	Rh(2)–C(9)–H(9)	127 (4)

the reactivity of such groups, in part due to their potential relationship to Fischer–Tropsch chemistry and to other hydrocarbon reactions catalyzed by metal surfaces.[1g,3] One important aspect, the interconversion of methylene with methyl or methylidyne groups, has been shown to occur intramolecularly in the $HOs_3(CO)_{10}(CH_3)/H_2Os_3(CO)_{10}(CH_2)/H_3Os_3(CO)_9(CH)$ system[4] and intermolecularly with the protonation of $Ru_2(PMe_3)_6(CH_2)_3$ to form $[Ru_2(PMe_3)_6(CH_2)_2(CH_3)]^+$.[1e] In examining related compounds, we have discovered that protonation of $Cp_2Rh_2(CO)_2(CH_2)$[1b] ($Cp \equiv \eta^5\text{-}C_5H_5$) leads to formation of a novel cationic methylidyne complex $[Cp_3Rh_3(CO)_2(CH)]^+$. The homologous ethylidyne complex $[Cp_3Rh_3(CO)_2(CCH_3)]^+$ is formed similarly from $Cp_2Rh_2(CO)_2(CHCH_3)$.[1b]

A CH_2Cl_2 solution of $Cp_2Rh_2(CO)_2(CH_2)$ (57 mg) was treated with excess CF_3COOH (135 μL), resulting in a dark solution. This was evaporated and the residue was dissolved in CH_3OH. Adding a saturated solution of KPF_6/CH_3OH precipitated $[Cp_3Rh_3(CO)_2(CH)]PF_6$ as a brown powder (31 mg, 61%). Crystals obtained from C_2H_6CO/CH_3OH at −78 °C appeared purple by transmitted light. Formulation of the compound as $[Cp_3Rh_3(\mu\text{-}CO)_2(\mu_3\text{-}CH)]PF_6$ has been established by spectroscopic data[5] [mass spectrum (field desorption), m/e 573 (M^+); IR (CH_2Cl_2) ν_{CO} 1927 (w), 1877 (w) cm^{-1}; ^1H NMR (C_2D_6CO, 30 °C) τ 4.13 (15 H, s), −6.20 (1 H, q, $J(Rh\text{-}H) = 2.4$ Hz)] and by a single-crystal X-ray diffraction study.[6]

The geometry of the $[Cp_3Rh_3(CO)_2(CH)]^+$ cationic complex is shown in Figure 1 and important interatomic distances and angles are given in Table I. The complex consists of a triangle of rhodium atoms, a triply bridging methylidyne group, two doubly bridging carbonyl ligands, and a normal $\eta^5\text{-}C_5H_5$ ring attached to each metal atom. The complex is bisected by a crystallographically imposed mirror plane, which contains Rh(1) and C(9)–H(9) and relates Rh(2) with Rh(2′) and C(10)–O(11) with C(10′)–O(11′). The rhodium-rhodium distances in the triangle differ very little (0.0074 Å) and are generally comparable with those found for related Rh_3[7] and Rh_2[1b] compounds. The $\eta^5\text{-}C_5H_5$ rings are tilted slightly toward the apical carbon atom, forming dihedral angles of 83.0° [ring bonded to Rh(1)] and 77.4° [rings bonded to Rh(2), Rh(2′)] with the Rh_3 plane. The carbonyl ligands are depressed below the Rh_3 plane by an angle of 64.3° and form distinctly asymmetric bridges, being 0.349 Å closer to Rh(2) and Rh(2′) than to Rh(1). This allows equalization of electron density between (if the bridges were symmetric) formally electron-rich Rh(1) and electron-poor Rh(2)/Rh(2′). The distances from the rhodium atoms to the methylidyne carbon atom, which is 1.212 Å above the Rh_3 plane, are only slightly different [0.036 Å *less* for Rh(1)–C(9)], despite the overall C_s symmetry of the complex. Furthermore, the C(9)–H(9) vector is nearly perpendicular to the Rh_3 plane.

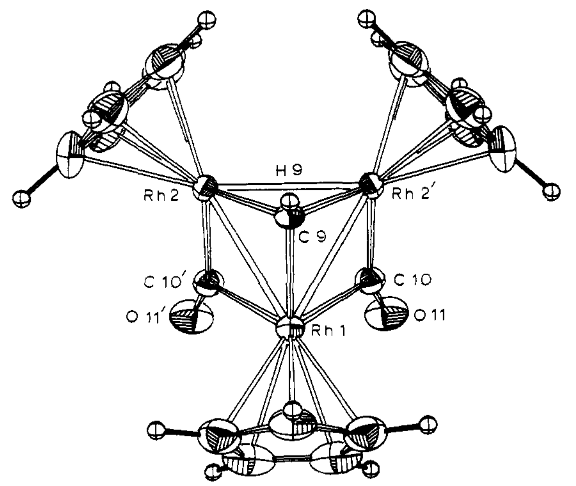

Figure 1. Geometry of the $[(\eta^5\text{-}C_5H_5)_3Rh_3(\mu\text{-}CO)_2(\mu_3\text{-}CH)]$ cation. In this view the crystallographic mirror plane is vertical.

The present structure is closely related to the structure of $Cp_3Co_3(\mu\text{-}CO)_2(\mu_3\text{-}CO)$,[8] which may be considered as the conjugate base of $Cp_3Co_3(\mu\text{-}CO)_2(\mu_3\text{-}COH)^+$. The reactivity implications of this comparison are being explored.

In solution the three rhodium atoms are rendered equivalent by a rapid carbonyl migration process. This is indicated by the quartet observed for the carbonyl ^{13}C NMR signal both at room temperature ($NCCD_3$, 203.6 ppm, $J(Rh\text{-}C)_{av} = 26$ Hz) and at −80 °C.

Protonation of $Cp_2Rh_2(CO)_2(CHCH_3)$ leads analogously to the ethylidyne cationic complex $[Cp_3Rh_3(CO)_2(CCH_3)]^+$, which has been isolated as the PF_6^- salt (38% yield) and characterized by spectroscopic data:[5] mass spectrum (field desorption), m/e 587, (M^+), 586 ($M^+ - H$), relative intensity 1:4; IR (CH_2Cl_2) ν_{CO} 1917 (m), 1877 (w) cm^{-1}; ^1H NMR (C_2D_6CO, 30 °C) τ 4.10 (15 H, br s), 5.07 (3 H, br s). Formation of the ethylidyne complex is significantly slower than of the methylidyne complex under similar conditions.

The stoichiometry of the reaction with trifluoroacetic acid has been established as shown in eq 1 by separate identification of

$$2Cp_2Rh_2(CO)_2(CHR) + H^+CF_3CO_2^- \rightarrow [Cp_3Rh_3(CO)_2(CR)]^+CF_3CO_2^- + CpRh(CO)_2 + CH_3R \quad (1)$$

$CpRh(CO)_2$ (IR and ^1H NMR) and CH_3R (GLC) (R = H, CH_3) as coproducts. We have not determined the initial site of attack by a proton on $Cp_2Rh_2(CO)_2(CHR)$, but an alkyl complex (methyl or ethyl) must be formed as an intermediate. Since we detected no *ethylene* in the case of R = CH_3, transfer of a second proton to the ethyl group and formation of ethane must be faster than loss of a proton and release of ethylene.

The involvement of two protons in the formation of alkane would be consistent with the results of Wilkinson and co-workers[1e] that protonation of $Ru_2(PMe_3)_6(CH_2)_2(CH_3)^+$ gives $Ru_2(PMe_3)_6(CH_2)_2^{2+}$ and methane. Furthermore, an explicit role for trifluoroacetate in coordinating to a reactive intermediate (perhaps $Cp_2Rh_2(CO)_2^{2+}$) is suggested by our initial results using the ether complex of fluoroboric acid as a proton source. In this case, the

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(2) For a recent review of synthetic aspects see: Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 800.

(3) For example, see: Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479.

(4) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 5225. *Ibid.* **1978**, *100*, 6544, 7726.

(5) Satisfactory elemental analyses also have been obtained.

(6) The compound crystallizes in the centrosymmetric orthorhombic space group *Pnma* with $a = 14.471$ (3) Å, $b = 10.959$ (2) Å, $c = 13.285$ (2) Å, $Z = 4$, $V = 2106.8$ Å^3, $F(000) = 1376$, and ρ(calcd) = 2.26 g cm^{-3} for MW = 718.05. Intensity data were collected with an automated Syntex $P2_1$ diffractometer (Mo Kα radiation) on a crystal of dimensions 0.45 × 0.55 × 0.55 mm ($\mu = 24.0$ cm^{-1}). Data in the quadrant $\pm h,k,l$ were collected in the θ–2θ scan mode out to $2\theta = 20°$ and the two nonunique octants were averaged, resulting in 3346 unique intensities which were considered significant at the $1.96\sigma(I)$ level. The data were corrected for Lorentz and polarization effects and the structure was solved by Patterson, difference Fourier, and full-matrix, least-squares refinement techniques. All atoms were located directly and included in the refinement. Using isotropic thermal parameters for the hydrogen atoms and anisotropic parameters for the nonhydrogen atoms established final agreement factors of $R = 0.044$ and $R_w = 0.054$.

The model also was tested in the acentric space group $Pna2_1$. The agreement factors necessarily were lower, but the resulting bond lengths and angles, particularly for the $\eta^5\text{-}C_5H_5$ and PF_6 moieties, deviated markedly from those expected.

(7) Paulus, E. F. *Acta Crystallogr., Sect. B* **1969**, *25*, 2206.

(8) Cotton, F. A.; Jamerson, J. D. *J. Am. Chem. Soc.* **1976**, *98*, 1273.

stoichiometry of which is still being studied, a high conversion to $Cp_3Rh_3(CO)_2(CR)^+$ appears to occur without formation of $CpRh(CO)_2$.[9]

Stirring a solution of $Cp_3Rh_3(CO)_2(CH)^+PF_6^-$ under an atmosphere of ^{13}CO at 40 °C leads to ^{13}CO enrichment without significant decomposition over ca. 2 days. More elevated temperatures, however, do lead to decomposition. Significantly, treatment of $Cp_3Rh_3(CO)_2(CH)^+$ with $LiHBEt_3$ under a CO atmosphere regenerates the $Cp_2Rh_2(CO)_2(CH_2)$, apparently by hydride attack at the methylidyne carbon; $CpRh(CO)_2$ and C_{3v} $Cp_3Rh_3(CO)_3$ are formed also. Additional reactions of these cationic alkylidyne complexes are being examined.

Acknowledgment. This work has been supported by a grant from the National Science Foundation and by fellowships from the A. P. Sloan Foundation and the Camille and Henry Dreyfus Foundation to J.R.S.

Supplementary Material Available: Tables listing atomic coordinates (Table A), bond lengths (Table B), bond angles (Table C), thermal parameters (Table D), and structure factors (Table E) (30 pages). Ordering information is given on any current masthead page.

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[9] As this work was being prepared for publication, we learned that Professor Herrmann and co-workers (Regensburg) also have observed the transformation of $Cp_2Rh_2(CO)_2(CH_2)$ into $[Cp_3Rh_3(CO)_2(CH)]^+$. Furthermore, they have obtained evidence that the reaction is initiated by protonation of the Rh–Rh bond, forming a hydrido–methylene complex, which then rearranges to a methyl species: Herrmann, W. A., et al. *Angew. Chem., Int. Ed. Engl.*, in press. Herrmann, W. A.; Plank, J.; Ziegler, M.; Balbach, B. *J. Am. Chem. Soc.* **1980**, *102*, 5908.

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Reaction of Diaryldiazomethanes with a Metal–Metal Triple Bond: Synthesis, Structural Characterizations, and Reactivity of Novel Bridging Diazoalkane and Alkylidene Complexes

Sir:

The reactions of diazoalkanes with organotransition-metal complexes, an area of growing interest,[1] have involved primarily mononuclear reactants. To our knowledge there have been no reported studies of diazoalkane reactions with metal–metal multiply bonded compounds. We wish to report the first example of such a reaction, in which the product has a new and unusual mode of diazoalkane coordination, and the clean conversion of the product to a novel species containing a bridging alkylidene[2] ligand. Although alkylidene complexes have been isolated previously from the reaction of diazoalkanes with metal complexes, our work also represents the first instance in which an intermediate diazoalkane complex has been characterized.

The reaction of $Cp_2Mo_2(CO)_4$[3] (**1**; Cp = η-C_5H_5) with either diphenyl- or bis(p-tolyl)diazomethane in CH_2Cl_2 at room temperature afforded in >90% yield the green diazoalkane adducts **2** (eq 1) which are air stable in the solid state.

$$\underset{\mathbf{1}}{\mathrm{Cp_2Mo_2(CO)_4}} + \mathrm{R_2CN_2} \rightarrow \underset{\substack{\mathbf{2a},\ \mathrm{R = Ph}\\ \mathbf{2b},\ \mathrm{R} = p\text{-}\mathrm{MeC_6H_4}}}{\mathrm{Cp_2Mo_2(CO)_4(N_2CR_2)}} \qquad (1)$$

Analogous complexes can be prepared from $(\eta$-$C_5H_4Me)_2Mo_2(CO)_4$. Elemental analysis, ^1H and ^{13}C NMR spectroscopy, and infrared spectroscopy[4] were consistent with this adduct formulation and suggested a structure, confirmed by single-crystal X-ray diffraction, with a diazoalkane bridge between the two molybdenum atoms. The principal features of the structure,[5] shown in Figure 1, are (1) a novel N(terminal) diazoalkane bridge with approximately planar coordination about N1, (2) asymmetry in the metal–bridge distances which suggests multiple bonding character in the Mo1–N1 bond, and (3) a semibridging[6] carbonyl group, trans to the diazoalkane bridge, which reduces charge asymmetry between the two singly bonded molybdenum atoms. N1 acts presumably as a four-electron donor,[7] with two electrons involved in a double bond to Mo1 and two electrons in a dative bond to Mo2; other canonical forms may contribute to the ground-state electronic structure. The adducts **2** are fluxional in solution on the ^1H and ^{13}C NMR time scales at room temperature, with a $\Delta G^\ddagger$ for cyclopentadienyl group equilibration in **2a** at the coalescence temperature (241 K) of 6.3 ± 0.1 kcal mol^{-1} as determined by variable-temperature ^1H NMR studies.

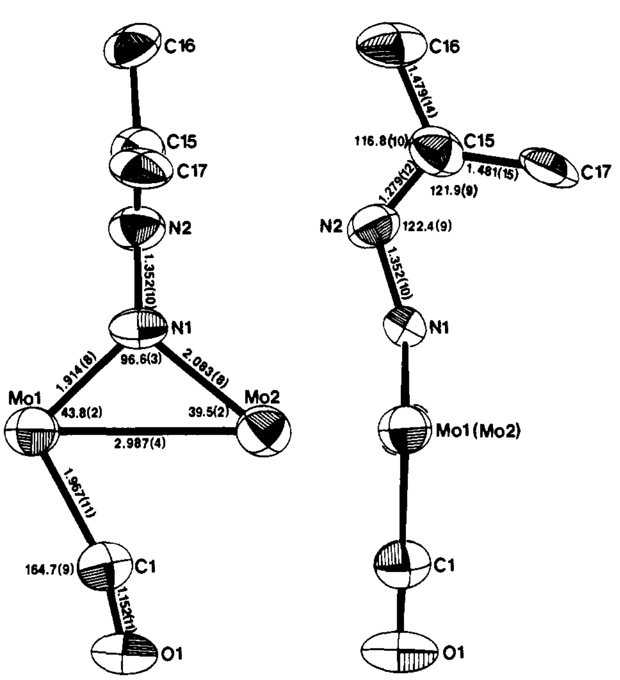

Figure 1. Two views of the molecular core of **2a**. The second view is obtained by rotating the first ~90° such that Mo1 is directly in front of Mo2. The Cp groups, the three remaining carbonyl groups, and all phenyl carbons except C_{ipso} are omitted for clarity. Bond distances are in angstroms, bond angles in degrees.

These adducts can be thermally decomposed in solution (C_6H_6, 60 °C) with loss of dinitrogen to afford the stable red μ-diarylmethylene complexes **3** (eq 2) in high yield. Their formulation

$$\mathrm{Cp_2Mo_2(CO)_4(N_2CR_2)} \xrightarrow{\Delta} \underset{\substack{\mathbf{3a},\ \mathrm{R = Ph}\\ \mathbf{3b},\ \mathrm{R} = p\text{-}\mathrm{MeC_6H_4}}}{\mathrm{Cp_2Mo_2(CO)_4(CR_2)}} + \mathrm{N_2} \qquad (2)$$

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[1] Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 800–812 and references therein.

[2] "International Union of Pure and Applied Chemistry, Nomenclature of Organic Compounds, Sections A, B, and C"; Butterworths: London, 1971; rule A.4.

[3] Klingler, R. J.; Butler, W. M.; Curtis, M. D. *J. Am. Chem. Soc.* **1978**, *100*, 5034–5039.

[4] Anal. Calcd for $Mo_2C_{27}H_{20}O_4N_2$: C, 51.60; H, 3.21; N, 4.46. Found: C, 50.41; H, 3.19; N, 4.16. ^1H NMR (δ, $C_6D_5CD_3$, −70 °C, 89.56 MHz) 4.69 (s, 5, Cp), 4.94(s, 5, Cp), 6.37–6.45(br d, 4, H_o), 6.85–7.78 (m, H_m and H_p); ^{13}C NMR (δ, $CDCl_3$, −38 °C, 22.5 MHz, $\{^1H\}$) 93.7 (s, CN_2), 95.5 and 97.3 (s, Cp and Cp′), 127.8, 128.5, 129.1, 131.5, 135.8, and 136.2 (s, Ph and Ph′), and 247 and 241 (br s, CO and CO′); IR (cm^{-1}, KBr) 1970 m, 1925 s, 1845 s, 1815 m (ν_{CO}), 1535 w $\nu_{C=N}$).

[5] **2a** crystallizes from a cooled CH_2Cl_2/C_6H_{14} solution in the monoclinic space group $P2_1/n$ (No. 13) with lattice constants a = 11.847 (4) Å, b = 10.407 (3) Å, c = 20.572 (6) Å, β = 97.81 (2)°, Z = 4, and V = 2513 (1) Å^3; ρ_{calcd} = 1.64 g cm^{-3}, ρ_{obsd} = 1.64 g cm^{-3} (flotation). The structure was refined to anisotropic convergence by using 2306 reflections with $I > 3\sigma(I)$; the final R value was 0.048 and the weighted R value was 0.059.

[6] (a) Curtis, M. D.; Han, K. R.; Butler, W. M. *Inorg. Chem.* **1980**, *19*, 2096–2101. (b) Cotton, F. A.; Kruczynski, L.; Frenz, B. A. *J. Organomet. Chem.* **1978**, *160*, 93–100.

[7] Curtis, M. D.; Klingler, R. J. *J. Organomet. Chem.* **1978**, *161*, 23–37.

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