Organometallic Chemistry of the Transition Metals. XIII. A π-Benzyl Derivative of Molybdenum with a Temperature-Dependent Proton Nuclear Magnetic Resonance Spectrum[1]

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Abstract: Reaction between $NaMo(CO)_3C_5H_5$ and benzyl chloride gives the yellow σ-benzyl derivative $C_6H_5CH_2$-$Mo(CO)_3C_5H_5$. Irradiation of this compound in hexane solution gives a low yield of the red π-benzyl derivative $C_6H_5CH_2Mo(CO)_2C_5H_5$. The temperature dependence of the proton nmr spectrum of this π-benzyl derivative is discussed. The proton nmr spectrum of the π-cycloheptatrienyl derivative $C_7H_7Mo(CO)_2C_5H_5$[2] was also found to be temperature dependent.

Numerous π-allyl derivatives of transition metals such as $[C_3H_5PdCl]_2$,[3] $C_3H_5Co(CO)_3$,[4,5] C_3H_5-$Mn(CO)_4$,[5,6] $C_3H_5Fe(CO)_3I$,[7-9] and $C_3H_5Mo(CO)_2$-C_5H_5[10] have been described. We wish now to report the first definite example[11] of a π-benzyl derivative in which *three* carbon atoms of the π-benzyl ligand, two of which are located in the benzene ring, are apparently complexed with the metal atom. The π-benzyl ligand is a benzolog of the π-allyl ligand, a relationship entirely analogous to that of the π-indenyl ligand and the π-cyclopentadienyl ligand and to that of naphthalene and benzene.

An originally unexpected property of this new π-benzyl derivative was the temperature dependence of its proton nmr spectrum. An analysis of this effect appears to clarify some of the anomalous features observed in the unexpectedly simple nmr spectra of several hydrocarbon–metal carbonyl complexes such as C_8H_8-$Fe(CO)_3$,[13] $C_7H_7Mo(CO)_2C_5H_5$,[2] $[C_7H_7Fe(CO)_3]^+$,[14] $[C_7H_7Fe_2(CO)_6]^+$,[15] and $C_8H_8Fe_2(CO)_5$.[16] In experiments suggested by our results we have also found the π-C_7H_7 portion of the proton nmr spectrum of C_7H_7Mo-$(CO)_2C_5H_5$ to be temperature dependent.

Experimental Section

Proton nmr spectra were taken in the indicated solvents using a Varian A-60 spectrometer equipped with a variable temperature

probe (lower temperature limit ∼−45°). Other general experimental techniques are adequately outlined in previous publications of this series.

Hexacarbonylmolybdenum was purchased from Climax Molybdenum Company. It was converted to $NaMo(CO)_3C_5H_5$ by treatment with a 20% excess of sodium cyclopentadienide in boiling tetrahydrofuran.[17] Sufficient $C_7H_7Mo(CO)_2C_5H_5$ remained from previous work[2,18] for observation of its nmr spectrum at −40°.

Preparation of the σ-Benzyl Derivative $C_6H_5CH_2Mo(CO)_3C_5H_5$. A mixture of 100 mmoles of $NaMo(CO)_3C_5H_5$ and 120 mmoles of benzyl chloride in 300 ml of tetrahydrofuran was stirred ∼16 hr at room temperature. After removal of the tetrahydrofuran at ∼25° (30 mm), the residue was extracted with three 100-ml portions of dichloromethane. Removal of solvent from the filtered dichloromethane extracts left yellow crystals of crude $C_6H_5CH_2$-$Mo(CO)_3C_5H_5$. These were extracted with ∼300 ml of boiling diethyl ether in three portions. Cooling the filtered yellow-orange diethyl ether solutions ∼16 hr at −78° precipitated yellow crystals. These were filtered and dried to give 22.38 g (67% yield) of yellow $C_6H_5CH_2Mo(CO)_3C_5H_5$ (I), mp 87–88°.

Anal. Calcd for $C_{15}H_{12}MoO_3$: C, 53.6; H, 3.6; O, 14.3; Mo, 28.6. Found: C, 52.7, 53.8; H, 3.6, 4.4; O, 14.7, 14.7; Mo, 26.9.

The infrared spectrum showed ν_{CO} (cyclohexane solution) 2025 (s) and 1947 (vs) cm⁻¹; remaining bands (KBr pellet) ν_{CH} at 3030 (vw), 2980 (vw), and 2920 (vw) cm⁻¹; other bands at 1586 (m), 1483 (m), 1445 (w), 1420 (m), 1411 (m), 1345 (vw), 1199 (w), 1150 (w), 1107 (vw), 1060 (w), 1057 (w), 1041 (vw), 1026 (vw), 1010 (m), 1000 (m), 995 (w), 974 (vw), 961 (vw), 922 (vw), 901 (w), 852 (w), 841 (vw), 830 (w), 818 (vs), 755 (vs), 724 (m), and 698 (s) cm⁻¹.

The proton nmr spectrum (CS_2 solution) showed singlet resonances at τ 2.87, 4.86, and 7.12 of approximate relative intensities 5:5:2 corresponding to the five phenyl protons, the five π-cyclopentadienyl protons, and the two methylene protons, respectively, in accord with structure I.

Preparation of the π-Benzyl Derivative $C_6H_5CH_2Mo(CO)_2C_5H_5$. A mixture of 10.0 g (29.7 mmoles) of the σ-benzyl derivative $C_6H_5CH_2Mo(CO)_3C_5H_5$ and 200 ml of n-hexane was exposed in a quartz tube to a 450-w ultraviolet lamp for 5 days. The yellow solid dissolved and a red-violet precipitate formed. After the reaction period was over, this precipitate of $[C_5H_5Mo(CO)_3]_2$ (2.26 g, 31% yield) was removed by filtration, washed with hexane (∼50 ml), and dried.

The hexane filtrate (∼250 ml) was cooled ∼16 hr at −78°. The resulting red mixture of π-$C_6H_5CH_2Mo(CO)_2C_5H_5$ and organic material was filtered and dried. It was then extracted with four 15-ml portions of benzene. The filtered red benzene solutions were chromatographed on a 5 × 50 cm alumina column. The chromatogram was developed with benzene. A yellow zone of

(1) For part XII of this series, see R. B. King, M. B. Bisnette, and A. Fronzaglia, *J. Organometal. Chem.* (Amsterdam), in press.

(2) (a) R. B. King and M. B. Bisnette, *Tetrahedron Letters*, 1137 (1963); (b) *Inorg. Chem.*, 3, 785 (1964).

(3) J. Smidt and W. Hafner, *Angew. Chem.*, 71, 284 (1959).

(4) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, 82, 750 (1960); 83, 1097 (1961).

(5) W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties, and B. W. Howk, *ibid.*, 83, 1601 (1961).

(6) H. D. Kaesz, R. B. King, and F. G. A. Stone, *Z. Naturforsch.*, 15b, 682 (1960).

(7) R. A. Plowman and F. G. A. Stone, *ibid.*, 17b, 575 (1962).

(8) H. D. Murdoch and E. Weiss, *Helv. Chim. Acta.*, 45, 1927 (1962).

(9) R. F. Heck and C. R. Boss, *J. Am. Chem. Soc.*, 86, 2580 (1964).

(10) M. Cousins and M. L. H. Green, *J. Chem. Soc.*, 889 (1963).

(11) Martin and Jellinek[12] have mentioned briefly the species $(C_5H_5)_2$-$TiCH_2C_6H_5$ allegedly containing a π-benzyl group. However, the paramagnetism of this titanium complex prevents the use of nmr spectroscopy required to establish unequivocally the π-benzyl structure in the absence of X-ray crystallographic data.

(12) H. A. Martin and F. Jellinek, *Angew. Chem.*, 76, 274 (1964).

(13) T. A. Manuel and F. G. A. Stone, *Proc. Chem. Soc.*, 90 (1959); *J. Am. Chem. Soc.*, 82, 366 (1960); M. D. Rausch and G. N. Schrauzer, *Chem. Ind.* (London), 957 (1959); A. Nakamura and N. Hagihara, *Bull. Chem. Soc. Japan*, 32, 880 (1919).

(14) J. E. Mahler, D. A. K. Jones, and R. Pettit, *J. Am. Chem. Soc.*, 86, 3589 (1964).

(15) G. F. Emerson, J. E. Mahler, R. Pettit, and R. Collins, *ibid.*, 86, 3590 (1964).

(16) C. E. Keller, G. F. Emerson, and R. Pettit, *ibid.*, 87, 1390 (1965).

(17) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 3, 104 (1956).

(18) The $C_7H_7Mo(CO)_2C_5H_5$ was stable on 2-year storage at −10° in a closed nitrogen-flushed bottle. The material used for the nmr spectrum had retained its characteristic orange color.
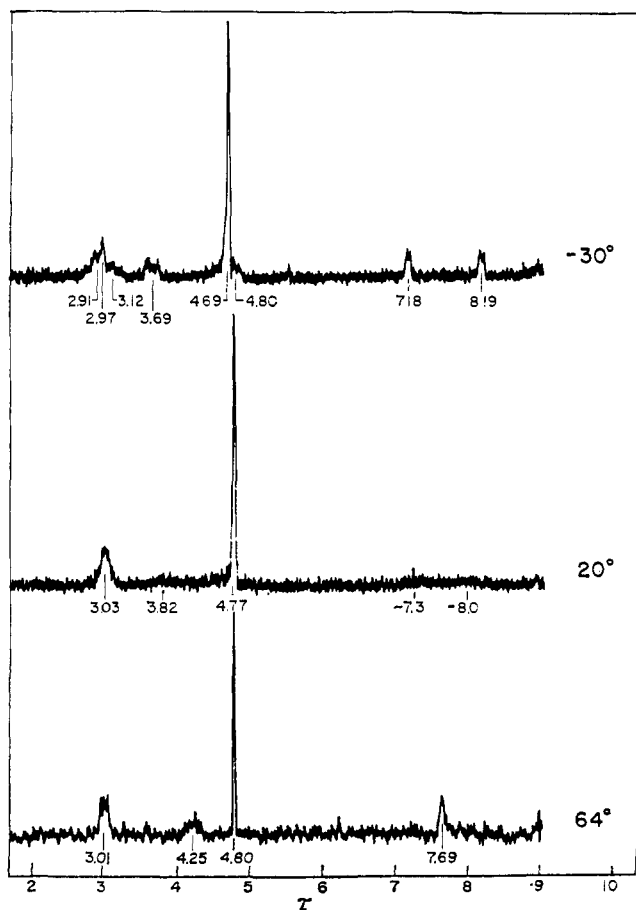
Figure 1. Temperature dependence of the proton nmr spectrum of π-C$_6$H$_5$CH$_2$Mo(CO)$_2$C$_5$H$_5$.

unchanged σ-C$_6$H$_5$CH$_2$Mo(CO)$_3$C$_5$H$_5$ followed by an incompletely separated red zone of π-C$_6$H$_5$CH$_2$Mo(CO)$_2$C$_5$H$_5$ was observed. Both of these zones were eluted with benzene, discarding the eluate from the portions of overlap between the yellow and red zones. Evaporation ($\sim$25° at 30 mm) of the filtered eluate from the yellow zone left yellow crystals. After one recrystallization from a mixture of pentane and diethyl ether 1.375 g (14% recovery) of yellow σ-C$_6$H$_5$CH$_2$Mo(CO)$_3$C$_5$H$_5$ was obtained.

The red eluate from the red zone left dark red crystals upon evaporation at $\sim$25° (30 mm). These were washed with three 15-ml portions of pentane and dried. Sublimation at 80° (0.1 mm) for $\sim$6 hr gave 0.492 g (5.4% yield) of dark red crystalline π-C$_6$H$_5$-CH$_2$Mo(CO)$_2$C$_5$H$_5$, mp 83–85°.

This π-benzyl derivative, π-C$_6$H$_5$CH$_2$Mo(CO)$_2$C$_5$H$_5$, was also obtained in $\sim$4% yield in apparently less pure condition as a dark red sublimate by heating the σ-benzyl derivative σ-C$_6$H$_5$CH$_2$-Mo(CO)$_3$C$_5$H$_5$ in a sublimer at $\sim$100° (0.1 mm).

The stability of π-C$_6$H$_5$CH$_2$Mo(CO)$_2$C$_5$H$_5$ was limited. Thus the red crystals gradually became black upon storage at room temperature in closed vials. Solutions in organic solvents oxidize noticeably after exposure to air for several minutes. A concentrated solution of π-C$_6$H$_5$CH$_2$Mo(CO)$_2$C$_5$H$_5$ in carbon disulfide in a closed nmr tube decomposed completely to blue-black insoluble material within 1 hr.

Anal. Calcd for C$_{14}$H$_{12}$MoO$_2$: C, 54.5; H, 3.9; Mo, 31.2; O, 10.4; mol wt, 308. Found: C, 55.3; H, 3.9; Mo, 30.7; O, 10.6; mol wt, 292 (osmometer in benzene solution).

The infrared spectrum showed ν_{CO} (cyclohexane solution)[19] 1965 (vw) and 1873 (m) cm^{-1}; ν_{CO} (halocarbon oil mull) 1954 (s), 1935 (s), 1833 (s) cm^{-1}; remaining bands (KBr pellet) ν_{CH} too weak to be unequivocally observed; other bands at 1596 (vw), 1528 (w), 1466 (w), 1439 (vw), 1417 (w), 1352 (vw), 1165 (vw), 1103 (vw),

1075 (w), 1053 (vw), 1003 (w), 969 (vw), 956 (vw), 868 (w), 810 (m), 796 (m), 767 (w), 744 (m), 717 (vw, br), and 693 (w) cm^{-1}.

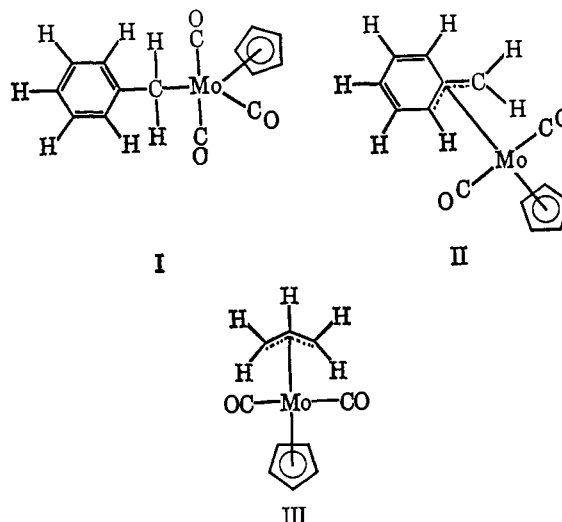The proton nmr spectra were taken in bromopentafluorobenzene solution at -30, -15, 0, $+20$, $+36$, $+40$, $+46$, $+52$, $+58$, $+64$, and $+70°$ and in trichlorofluoromethane solution at -45, -30, -15, and 0°. Representative spectra are depicted in Figure 1.

Discussion

Many π-allyl derivatives of metal carbonyls such as C$_3$H$_5$Co(CO)$_3$,[4,5] C$_3$H$_5$Mn(CO)$_4$,[5,6] C$_3$H$_5$FeCOC$_5$H$_5$,[20] C$_3$H$_5$Mo(CO)$_2$C$_5$H$_5$,[10] and C$_3$H$_5$W(CO)$_2$C$_5$H$_5$[21] are prepared by elimination of 1 mole of carbon monoxide from the corresponding σ-allyl derivative by pyrolysis or photolysis. The preparation of the π-benzyl derivative π-C$_6$H$_5$CH$_2$Mo(CO)$_2$C$_5$H$_5$ from the σ-benzyl derivative σ-C$_6$H$_5$CH$_2$Mo(CO)$_3$C$_5$H$_5$ (I) is exactly analogous but proceeds in lower yield.

Of unusual interest was the temperature-dependent proton nmr spectrum of the π-benzyl derivative π-C$_6$H$_5$CH$_2$Mo(CO)$_2$C$_5$H$_5$ (Figure 1). On the basis of the relative intensities and chemical shifts, the generally complexly split resonances at τ 2.91, 2.97, 3.12, 3.69, and 4.80 in the spectrum at $-30°$ may be assigned to the five aromatic protons which are thus nonequivalent as required for the expected π-benzyl structure II. The two nonequivalent equally split ($J = 3$ cps) doublets at τ 7.18 and 8.19 in the spectrum at $-30°$ may be assigned to the two coupled, nonequivalent methylene protons of the π-benzyl group as also required for the π-benzyl structure II. Finally the sharp singlet at τ 4.69 may be assigned to the five equivalent π-cyclopentadienyl protons. The nmr spectrum of π-C$_6$H$_5$-CH$_2$Mo(CO)$_2$C$_5$H$_5$ at $-30°$ is thus completely in accord with that expected for the π-benzyl structure II, entirely analogous to the accepted structure III for the π-allyl derivative C$_3$H$_5$Mo(CO)$_2$C$_5$H$_5$.[10]

Upon warming the solution of π-C$_6$H$_5$CH$_2$Mo-(CO)$_2$C$_5$H$_5$, the nmr spectrum undergoes marked reversible changes (Figure 1). In the extreme case exhibited at $+64°$, the two methylene protons appear as a broad singlet at τ 7.69, which is the mean value of the chemical shifts of the two doublets observed for the methylene protons in the low-temperature spectrum. Also at $+64°$ the two aromatic protons which appear

I

II

III

(19) This cyclohexane solution also exhibited considerably weaker bands at 2025 and 1947 cm.$^{-1}$, correponding to a small quantity of σ-C$_6$H$_5$CH$_2$Mo(CO)$_3$C$_5$H$_5$ apparently present as a decomposition product.

(20) M. L. H. Green and P. L. I. Nagy, *J. Chem. Soc.*, 189 (1963).

(21) M. L. H. Green and A. N. Stear, *J. Organometal. Chem.* (*Amsterdam*), **1**, 230 (1964).

at τ 3.69 and 4.80 in the low-temperature spectrum have coalesced into a broad resonance again at the mean value of τ 4.25. Finally at $+64°$ the two aromatic protons which appeared at τ 2.91 and 3.12 in the low-temperature spectrum appear to have similarly coalesced into a complex resonance overlapping with that of the one remaining aromatic proton.

For discussion of the temperature dependence of the nmr spectrum of this π-benzyl derivative, it is first helpful to consider the related π-allyl derivatives. X-Ray structural studies on $[C_3H_5PdCl]_2$[22,23] suggest all of the carbon and hydrogen atoms of the π-C_3H_5 ligand to be coplanar. However, the palladium atom is so situated with respect to the π-C_3H_5 ligand that the two methylene hydrogen atoms on each of the two equivalent end carbon atoms are different distances from the palladium atom, accounting for their different chemical shifts in the proton nmr spectrum.[24]

Analogy with such π-allyl complexes suggests that the carbon and hydrogen atoms of the π-benzyl ligand in π-$C_6H_5CH_2Mo(CO)_2C_5H_5$ are coplanar, at least at $-30°$. Again the nonequivalent chemical shifts of the methylene protons arise from their different distances to the molybdenum atom.

However, the planar π-benzyl ligand (IV) can rotate around an axis passing through carbon atoms 4, 1, and 7. Rotation of this ligand $180°$ about this axis produces a π-benzyl complex indistinguishable from the original complex except that the three carbon atoms 6, 1, and 7 rather than the three carbon atoms 2, 1, and 7 are bonded to the metal atom.

Rotation about this axis of carbon atoms 4, 1, and 7 provides one possible explanation for the temperature dependence of the proton nmr spectrum of π-C_6H_5-$CH_2Mo(CO)_2C_5H_5$. At low temperatures (*e.g.*, $-30°$) this rotation does not occur and the nmr spectrum is that expected for the "fixed" π-benzyl structure II as already discussed above. However, when the temperature is raised, rotation about this axis of carbon atoms 4, 1, and 7 occurs at an increasing rate. Finally at $+64°$ the rotation is occurring sufficiently fast that the originally nonequivalent methylene protons appear equivalent within the time restriction of the nmr spectrometer and thus exhibit a single resonance at the mean value. Furthermore, rapid rotation about the axis of carbon atoms 4, 1, and 7 makes carbon atom 3 equivalent to carbon atom 5 and carbon atom 2 equivalent to carbon atom 6. The attached protons thus become equivalent in accord with the observed spectrum at $+64°$. The coalescence of the six resonances from three nonequivalent pairs of protons at $-30°$ into three resonances at $+64°$ at exactly the *mean* values of the three original pairs supports this rotation mechanism as opposed to other types of reversible chemical changes. Also *unlike* certain other possible rotation mechanisms (*e.g.*, those involving rotation about an axis collinear with the molybdenum atom and any of the carbon atoms of the π-benzyl ligand), the proposed rotation mechanism about the axis of carbon atoms 4, 1, and 7 makes the methylene protons equivalent when the rate of rotation is sufficiently great (as at $+64°$).
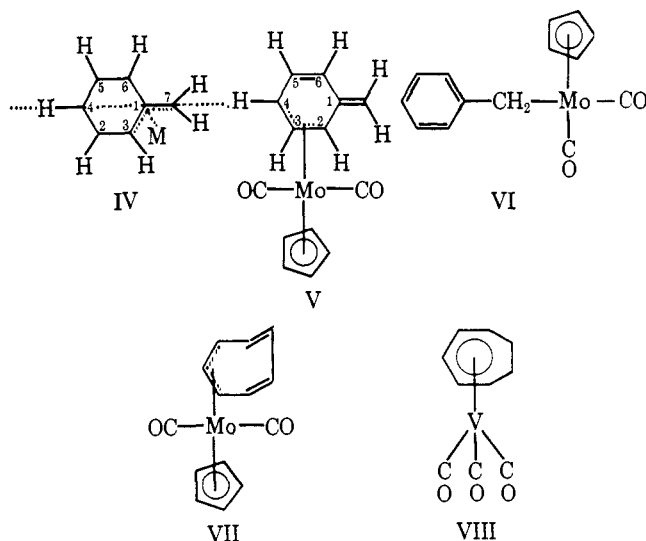
Other mechanisms may be postulated for making equivalent at higher temperatures the two methylene protons, carbon atoms 3 and 5, and carbon atoms 2 and 6. One possibility is a *revolution* mechanism[25] where the $-Mo(CO)_2C_5H_5$ group revolves around the ring. In this mechanism the $-Mo(CO)_2C_5H_5$ group is bonded successively to carbon atoms 2, 1, and 7; 4, 3, and 2 (V); 4, 5, and 6; and 6, 1, and 7, respectively. Another possibility[26] is the rapid interconversion at higher temperatures of the π-benzyl derivative with the $-Mo(CO)_2C_5H_5$ group bonded to carbon atoms 2, 1, and 7 to the π-benzyl derivative with the $-Mo(CO)_2C_5H_5$ group bonded to carbon atoms 6, 1, and 7 through the σ-benzyl intermediate VI in which the $-Mo(CO)_2C_5H_5$ group is bonded only to carbon atom 7 (*"end-run"* mechanism). This σ-benzyl intermediate VI, unlike the σ-benzyl derivative I characterized in detail in this paper, has a molybdenum atom with two electrons less than the favored rare gas configuration. Unfortunately, the temperature dependence of the proton nmr spectrum of π-$C_6H_5CH_2Mo(CO)_2C_5H_5$ does not permit an unequivocal distinction between the rotation, revolution, and "end-run" mechanisms for making the two methylene protons, carbon atoms 3 and 5, and carbon atoms 2 and 6 equivalent at higher temperatures such as $+64°$.

By the technique developed by Gutowsky and Holm[27] and used by Cramer[28] for $C_5H_5Rh(C_2H_4)_2$, it is possible to estimate the energy of activation for the rotation from the temperature dependence of the nmr spectrum. For π-$C_6H_5CH_2Mo(CO)_2C_5H_5$ a value of ~ 6 kcal is thus obtained in bromopentafluorobenzene solution. Unfortunately, however, small errors in the chemical shift measurements at certain temperatures lead to large errors in the experimentally determined energy of activation by the Gutowsky–Holm technique. Thus in π-$C_6H_5CH_2Mo(CO)_2C_5H_5$ an error of only ± 0.5 cps in the measured chemical shift at $-15°$ results in an error of $\sim \pm 30\%$ in the resulting energy of activation.

(22) W. E. Oberhansli and L. F. Dahl, *J. Organometal. Chem.* (*Amsterdam*), **3**, 43 (1965).
(23) A. E. Smith, *Acta Cryst.*, **18**, 331 (1965).
(24) H. C. Dehm and J. C. W. Chien, *J. Am. Chem. Soc.*, **82**, 4429 (1960).
(25) We are indebted to a referee who made suggestions leading to the postulation of this revolution mechanism.
(26) We are indebted to Professor R. Pettit of the University of Texas who suggested this "end-run" mechanism in discussions at the Second International Symposium on Organometallic Chemistry, Madison, Wis., Sept 1, 1965.
(27) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).
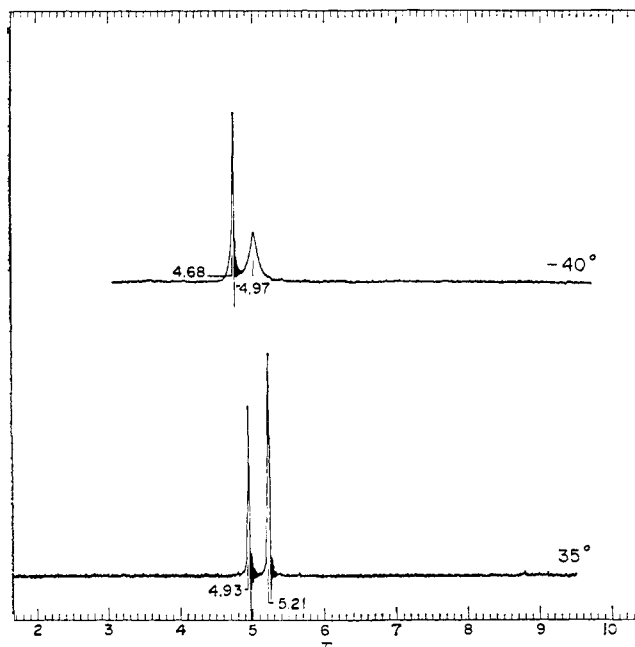(28) R. Cramer, *J. Am. Chem. Soc.*, **86**, 217 (1964).

Figure 2. Temperature dependence of the proton nmr spectrum of π-$C_7H_7Mo(CO)_2C_5H_5$.

These studies have shown the π-benzyl derivative π-$C_6H_5CH_2Mo(CO)_2C_5H_5$ (II) to be the first example of a transition metal carbonyl π complex of a carbocyclic system which may exhibit either the nmr spectrum of a "frozen" structure or of a freely rotating structure depending upon the temperature. Similar[29] free rotation of a metal atom about a π-cyclopentadienyl or π-cyclooctatetraene ring has been suggested frequently to account for the anomalous single sharp resonances in $C_8H_8Fe(CO)_3$ and related compounds where chemical[2,13-16] and X-ray crystallographic[30] studies suggest the carbon atoms and thus the hydrogen atoms of the π-C_7H_7 or π-C_8H_8 ligands to be nonequivalent. However, cooling of solutions of these π-C_7H_7 or π-C_8H_8 complexes sufficiently for the anomalous single resonances to diverge into the more "normal" complex patterns indicative of hindrance of the postulated rotation has not yet been reported.[31]

In an attempt to observe broadening due to restriction of the postulated rotation, the proton nmr spectra of $C_8H_8Fe(CO)_3$ and $C_7H_7Mo(CO)_2C_5H_5$ were taken at $-40°$ in chloroform solution. The spectrum of $C_8H_8Fe(CO)_3$ at $-40°$ exhibited a single, sharp resonance identical with that exhibited at ambient temperature. However, in $C_7H_7Mo(CO)_2C_5H_5$ (VII) (Figure 2) the π-C_7H_7 resonance was 5.3 times broader relative to the π-C_5H_5 resonance at $-40°$ than at room temperature.[33,34] The comparison with the π-C_5H_5 resonance excludes the possibility of this broadening of the π-C_7H_7 resonance arising from inferior resolution at the low temperature or other similar features of spectrometer operation. The broadening of the π-C_7H_7 resonance in $C_7H_7Mo(CO)_2C_5H_5$ at low temperatures thus appears to be an inherent characteristic of the compound presumably arising from hindrance of the position-equalizing rotation of the allylic[35] π-cycloheptatrienyl ring. The temperature dependences of the π-C_7H_7 resonance in the allylic[35] π-cycloheptatrienyl derivative $C_7H_7Mo(CO)_2C_5H_5$ (broad at low temperatures and sharp at higher temperatures) and in the planar[35] π-cycloheptatrienyl derivative $C_7H_7V(CO)_3$ (VIII) (sharp at low temperatures and broad at higher temperatures) are exactly reversed, confirming the original postulation[2] of different types of bonding of the π-C_7H_7 ring in these two compounds.

After the work described in this paper was complete, a report by Winstein, Kaesz, Kreiter, and Friedrich[36] mentioned the preparation of the π-cyclooctatetraene complex $C_8H_8Mo(CO)_3$. The proton nmr spectrum of $C_8H_8Mo(CO)_3$ exhibits a similar temperature dependence to that depicted in Figure 2 for $C_7H_7Mo(CO)_2$-C_5H_5. However, the C_8H_8 resonance of $C_8H_8Mo(CO)_3$ already was broad at room temperature where the C_7H_7 resonance of $C_7H_7Mo(CO)_2C_5H_5$ was sharp.

tures and broad at *high* temperatures in a manner opposite to that expected for restriction of rotation by a temperature decrease. The bonding of the planar π-cycloheptatrienyl ring in $C_7H_7V(CO)_3$ is entirely different from that postulated for the allylic π-cycloheptatrienyl rings in $C_7H_7Mo(CO)_2C_5H_5$ and $C_7H_7Co(CO)_3$.[2]

(29) The rotations postulated for π-benzyl complexes and π-cycloheptatrienyl or π-cyclooctatetraene complexes are similar in involving rotation in a π-bonded cyclic hydrocarbon ligand. However, the axes of rotation in these two types of complexes are very different. The rotation axis for π-cycloheptatrienyl or π-cyclooctatetraene complexes in order to make the seven or eight hydrogen atoms equivalent in accord with the observed nmr spectra must pass through the center of the ring and be equidistant to all seven or eight carbon atoms. In contrast to the rotation axis in π-benzyl complexes, the rotation axis in π-cycloheptatrienyl or π-cyclooctatetraene complexes cannot pass through any of the ring carbon atoms.

(30) B. Dickens and W. N. Lipscomb, *J. Chem. Phys.*, 37, 2084 (1962).

(31) Fritz and Kreiter[32] have found the π-C_7H_7 resonance of the planar π-cycloheptatrienyl derivative $C_7H_7V(CO)_3$ to be temperature dependent. However, this π-C_7H_7 resonance is sharp at *low* tempera-

(32) H. P. Fritz and C. G. Kreiter, *Ber.*, 97, 1398 (1964).

(33) Because of an error somewhere in the process of manuscript preparation, the description of the nmr spectrum of $C_7H_7Mo(CO)_2C_5H_5$ in one location in ref 2b was reversed. Page 787, column 2, line 49 of this reference should be corrected to read as follows: "Proton N.M.R. Spectrum.—Sharp cyclopentadienyl resonance at τ 4.93 and sharp cycloheptatrienyl resonance at τ 5.21 of relative intensity ~5:7 (carbon disulfide solution)."

(34) In the spectrum of $C_7H_7Mo(CO)_2C_5H_5$ at $-40°$ the assignments of the sharp resonance at τ 4.68 to the five π-cyclopentadienyl protons and the broad resonance at τ 4.97 to the seven π-cycloheptatrienyl protons were confirmed by integration.

(35) For a description of the use of the terms "planar π-cycloheptatrienyl" and "allylic π-cycloheptatrienyl," see footnote 24 in ref 2b.

(36) S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *J. Am. Chem. Soc.*, 87, 3267 (1965).