N–O bond decreases upon coordination. The fact that the N–O frequency of the aliphatic amine N-oxides shows little or no shift on coordination can be attributed to the single-bond character of the N–O bond. Coordination relieves the electron density around the oxygen but has little effect on the N–O bond.

Experimental Section

Preparation.—The ligand *p*-bromodimethylaniline N-oxide was prepared by oxidizing *p*-bromodimethylaniline with hydrogen peroxide and acetic acid. The complexes were prepared by adding an acetone solution of the ligand to an acetone–dimethoxypropane solution of the metal salt. The complexes usually formed when stirred for several minutes.

Physical Measurements.—The infrared spectra were taken as Nujol mulls on a Beckman IR5A recording spectrophotometer with NaCl optics. The visible spectra were obtained with a Cary Model 14 recording spectrophotometer. Conductance data were obtained using a conductance bridge manufactured by Industrial Instruments Inc. The decomposition products were studied with the aid of thin layer chromatography.

Analyses.—Carbon, hydrogen, and nitrogen analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Mülheim, West Germany.

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Correspondence

Stereochemically Nonrigid Organometallic Compounds. VI. Configurational Equilibria of π-$C_5H_5Mo(CO)_2$ Allyl Complexes

Sir:

Recently evidence has been presented[1,2] that the temperature dependence of the nmr spectra and their eventual collapse to dynamic A_4X spectra of certain π-allyl complexes is due to a rapid exchange between a π-bonded group and a short-lived σ-bonded intermediate. In certain isoleptic π-allyl complexes, such as $Zr(\pi\text{-}C_3H_5)_4$ and $Pd(\pi\text{-}C_3H_5)_2$, Becconsall, *et al.*,[3] and Wilke, *et al.*,[4] have rationalized the temperature-dependent spectra as resulting from internal rotation of the CH_2 protons about the C–C bond which leads to an averaging of the *syn* and *anti* protons to give A_4X spectra. The former authors rejected a σ–π interconversion on their misinterpretation[3b] of their incompletely averaged high-temperature spectrum of $Pd(\pi\text{-}C_3H_5)_2$. It has been pointed out that other mechanisms can lead to temperature-dependent spectra for π-allyl ligands: either rotation of the π-allyl about an axis through the C–C–C plane[1] or a mechanism involving a flip through a planar intermediate.[5] The former mechanism does not interconvert the *syn* and *anti* protons of the allyl ligand, is clearly operative in the case of $Rh(\pi\text{-}C_3H_5)_3$, and is very probable in the case of $Pd(\pi\text{-}C_3H_5)_2$ although the data cited are insufficient.[3] King[6] has claimed that the existence of four infrared carbonyl stretching frequencies in $(\pi\text{-}C_5H_5)Mo(CO)_2(\pi\text{-}C_3H_5)$ and similar species is due to the presence of *cis* and *trans* isomers based on a piano stool arrangement of the allyl ligand and the two carbonyl groups about the $(\pi\text{-}C_5H_5)Mo$ moiety. We present evidence which shows that for $(\pi\text{-}C_5H_5)Mo(CO)_2(\pi\text{-}C_3H_5)$ a more reasonable interpretation is one involving a configurational equilibrium between species which in a formal sense could be regarded as conformers. We reject the presence of *cis* and *trans* isomers for the following reasons: (i) It seems unreasonable from steric considerations to have the π-C_3H_5 group occupying the *trans* positions, but even more unlikely for the case of the C_7H_7 group in $(\pi\text{-}C_5H_5)Mo(CO)_2(\pi\text{-}C_7H_7)$, which also shows four infrared-active carbonyl stretching modes. (ii) From numerous studies of the vibrational spectra of metal carbonyls, it is known that the interaction constants k_c and k_t between pairs of *cis* and *trans* CO groups obey the approximate relationship $k_t \approx 2k_c$.[7] This leads to a marked difference between the separation of the symmetric and antisymmetric stretching modes in the *cis* and *trans* isomers, contrary to that observed in this case. (iii) The variable-temperature nmr spectra of Figure 1 show quite clearly that at low temperature (*ca.* −10 to −50°) the interconversion is slow enough to distinguish two distinct π-allyl groups and that these become averaged to a spectrum typical of a π-allyl (*i.e.*, AA′BB′X) at +130°.

The temperature dependence was essentially[8] the same in $CDCl_3$ and C_6H_6 throughout the range from +10 to +40°. However, spectra could not be obtained over the entire range in chlorinated solvents because of rapid decomposition at temperatures greater than *ca.* +50°. It is clear that the averaging process at +130°

[1] F. A. Cotton, J. W. Faller, and A. Musco, *Inorg. Chem.*, **6**, 179 (1967).

[2] K. Vrieze, C. MacLean, P. Cossee, and C. W. Hilbers, *Rec. Trav. Chim.*, **85**, 1077 (1966).

[3] (a) J. K. Becconsall, B. E. Job, and S. O'Brien, *J. Chem. Soc., Sect. A*, 423 (1967); (b) the broadening and partial collapse of the nmr spectra of $Pd(\pi\text{-}C_3H_5)_2$ in the incompletely averaged range (*ca.* +30–70°) was suggested to be due to the onset of the internal rotation mechanism. Since the limiting spectrum was not observed, no valid conclusions can be drawn but there is a remarkable similarity between this behavior and that for $(\pi\text{-}C_5H_5)Mo(CO)_2(\pi\text{-}C_3H_5)$.

[4] G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kroner, W. Oberkirch, K. Tanaka, and D. Walter, *Angew. Chem. Intern. Ed. Engl.*, **5**, 151 (1966).

[5] *Cf.* the discussions of the article by G. Wilke, *et al.*, in "Proceedings of the 9th Robert A. Welch Conference on Chemical Research, Nov 15–17, 1965," especially those by F. A. Cotton, p 184.

[6] R. B. King, *Inorg. Chem.*, **5**, 2242 (1966).

[7] F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).

[8] Solvent shifts for the various environments were observed in these spectra.

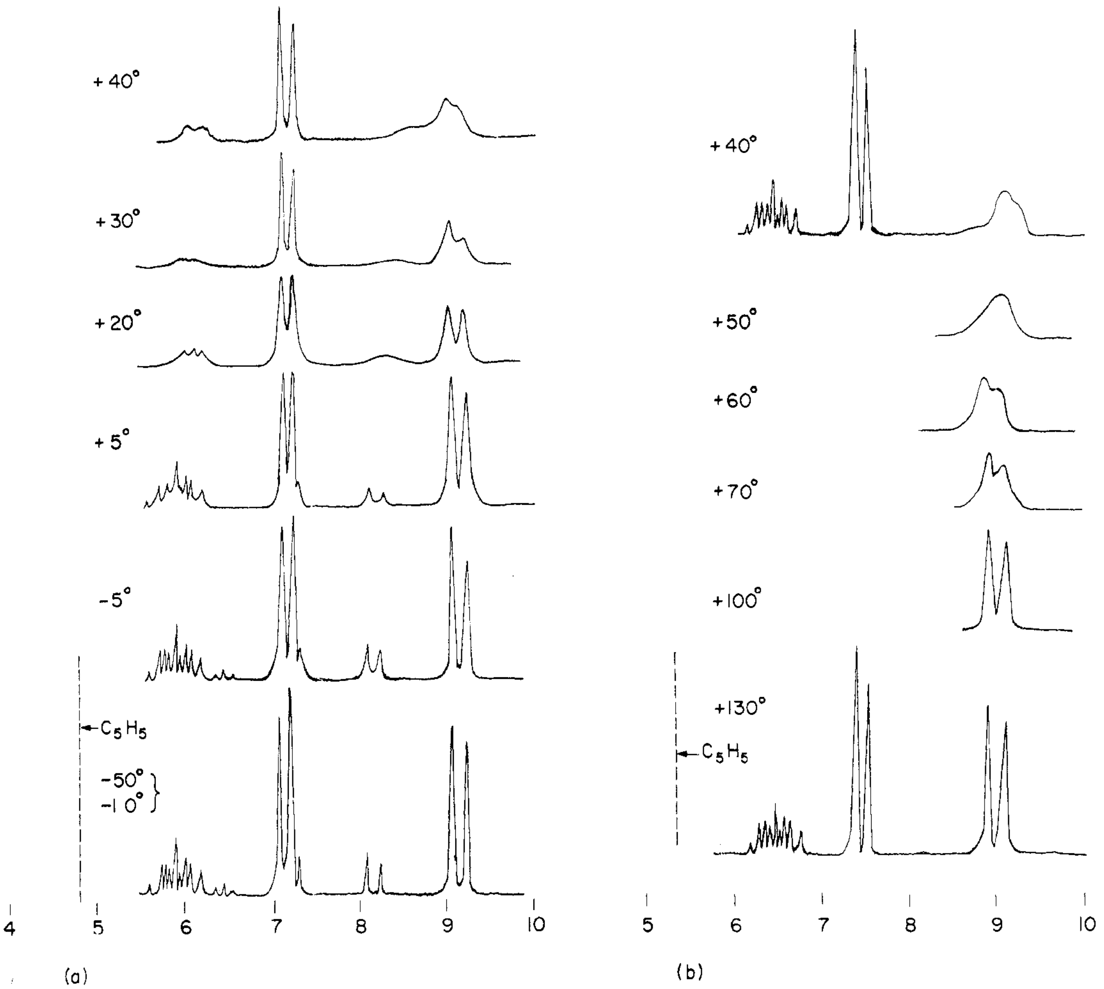

Figure 1.—The temperature dependence of the nmr spectra of (π-C_5H_5)Mo(CO)$_2$(π-C_3H_5), (a) in $CDCl_3$ and (b) in C_6H_6. The high-temperature spectra were obtained using sealed tubes on a Varian A-60 spectrometer equipped with a variable-temperature probe.

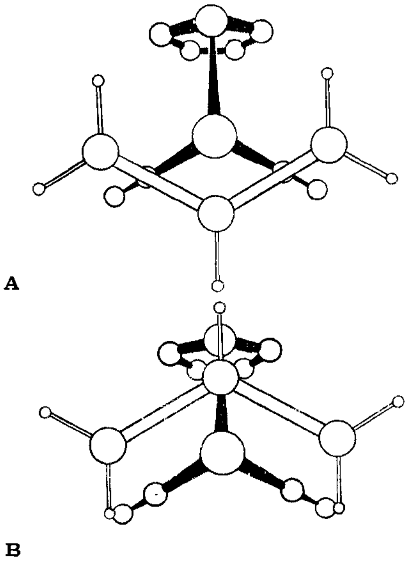

Figure 2.—Probable configurations of (π-C_5H_5)Mo(CO)$_2$-(π-C_3H_5). The cyclopentadienyl protons have been omitted for simplicity.

involves an equilibrium between different configurations, which is rapid compared to the nmr time scale. At low temperatures two isomers exist in unequal amounts (*ca.* 1:7). While we cannot specify the exact mechanism for the interconversion (*i.e.*, rotation about an axis through the C–C–C plane or an equivalent operation which does not interconvert the *syn* and *anti* protons), we feel that the two most likely structures for the species are those shown in Figure 2, with 2A most probably being the more stable.[9]

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[10] NSF Student Participant, 1966–1967.

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On the Electronic Structure of the Tris(2,2′-bipyridyl)chromium(II) Ion

Sir:

In an earlier paper[1] we reported the magnetic susceptibility at several temperatures for the low-spin d^4 complex, tris(2,2′-bipyridyl)chromium(II) bromide tetra-

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[1] A. Earnshaw, L. F. Larkworthy, K. C. Patel, K. S Patel, R. L. Carlin and E. G. Terezakis, *J. Chem. Soc., Sect. A*, 511 (1966).