-13 cm^{-1} for the strong band at 1382 cm^{-1}, and -24 cm^{-1} for the medium band at 1257 cm^{-1}. The strong bands at 1685 and 1083 cm^{-1} were unaffected by the N^{15} substitution.[20] Occam's razor brings us to the conclusion that, if group frequency approximations must be applied, assignment III above is favored.

The data of Table II, however, in conjunction with the valence bond picture, constitute *prima facie* evidence for some coupling of ν(C—N) and ν(C′—N) with ν(C=O), *i.e.*, for the group frequency approximation being inadmissible here. Further work on other isotopomeric amide pairs is in progress.

Acknowledgments.—Our work is supported by the Advanced Research Projects Agency. We thank R. E. Hester for helpful discussions.

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[20] M. R. Bramwell, E. W. Randall, and J. J. Zuckerman, unpublished results.

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RECEIVED JUNE 6, 1966

The Differentiation between Unidentate and Bidentate Ligands Which Donate Three Electrons to a Metal Atom[1]

Sir:

During the last three years, work from this laboratory has resulted in the preparation and study of several new compounds of the general type $C_5H_5M(CO)_2T$ (M = Mo or W; T = neutral[2] ligand donating three electrons to a metal atom).[3] In compounds of this type it is possible for the three-electron donor ligand to be of several types[4] including the following: (a) unidentate occupying one coordination position of the metal atom through which the net donation of all three electrons occurs and (b) bidentate occupying two coordination positions of the metal atom. Donation of two of these three electrons occurs through one of the coordination positions and donation of the third electron occurs through the other coordination position. In a further comparative study of the infrared spectra of various $C_5H_5M(CO)_2T$ compounds in the metal carbonyl stretching region under high-resolution conditions[5,6] we have found an apparent means of differentiating between $C_5H_5M(CO)_2T$ compounds containing unidentate T ligands and those containing bidentate T ligands.[7]

Compounds of the type $C_5H_5M(CO)_2T$ (M = Mo or W) are expected to exhibit two metal carbonyl stretching frequencies. These predicted two frequencies are indeed observed (Table I) for those $C_5H_5M(CO)_2T$ compounds where T must clearly be monodentate (*i.e.*, the nitrosyl $C_5H_5Mo(CO)_2NO$). However, other $C_5H_5M(CO)_2T$ compounds such as the π-allyl derivative $C_5H_5Mo(CO)_2C_3H_5$ exhibit *four strong* metal carbonyl stretching frequencies (Table I). Since these four strong frequencies are observed in solution, they clearly cannot arise from solid-state effects. Since any possible single structure for $C_5H_5Mo(CO)_2C_3H_5$ can exhibit only two metal carbonyl stretching frequencies, the presence of four strong metal carbonyl frequencies indicates the presence of two different species in solution.[8]

TABLE I

METAL CARBONYL STRETCHING FREQUENCIES OF $TM(CO)_2C_5H_5$ COMPOUNDS (CM^{-1})[a]

A. Compounds Exhibiting Two Metal Carbonyl Stretching Frequencies

$C_5H_5Mo(CO)_2NO$	2021 s, 1948 vs
$C_5H_5W(CO)_2NO$	2011 s, 1935 s
$C_6H_5N_2Mo(CO)_2C_5H_5$	2000 s, 1928 s
p-$CH_3C_6H_4N_2Mo(CO)_2C_5H_5$	1997 s, 1925 s
p-$O_2NC_6H_4N_2Mo(CO)_2C_5H_5$	2010 s, 1942 s
π-$CH_3SCH_2Mo(CO)_2C_5H_5$	1952 s, 1869 s
π-$CH_3SCH_2W(CO)_2C_5H_5$	1941 s, 1856 s
π-$C_6H_5CH_2Mo(CO)_2C_5H_5$	1965 vs, 1873 m

B. Compounds Exhibiting Four Metal Carbonyl Stretching Frequencies

π-$C_3H_5Mo(CO)_2C_5H_5$	1970 s, 1963 s, 1903 s, 1889 s
π-$C_7H_7Mo(CO)_2C_5H_5$	1968 s, 1962 s, 1915 s, 1900 s
π-$C_7H_7W(CO)_2C_5H_5$	1967 s, 1958 s, 1910 s, 1893 s

[a] Cyclohexane solution, Beckman IR-9 spectrometer; estimated error in frequencies $< \pm 2$ cm^{-1}.

If the π-allyl ligand in $C_5H_5Mo(CO)_2C_3H_5$ occupies two coordination positions, two isomers are clearly possible. X-Ray crystallographic studies[9] have shown

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[1] The author is indebted to the Air Force Office of Scientific Research for partial support of this work under Grant AF-AFOSR-580-66.

[2] It is most convenient to regard such complexes as formed from neutral ligands and metal atoms. This is in accord with the formal structure of coordination chemistry presented by the author at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

[3] For preparation of the compounds discussed in this paper, see the following references: (a) $C_5H_5M(CO)_2NO$ (M = Mo or W): T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956); E. O. Fischer, O. Beckert, W. Hafner, and H. O. Stahl, *Z. Naturforsch.*, **10b**, 598 (1955); (b) $RN_2Mo(CO)_2C_5H_5$: R. B. King and M. B. Bisnette, *Inorg. Chem.*, **5**, 300 (1966); (c) π-$CH_3SCH_2M(CO)_2C_5H_5$ (M = Mo or W): R. B. King and M. B. Bisnette, *ibid.*, **4**, 486 (1965); (d) π-$C_3H_5Mo(CO)_2C_5H_5$: M. Cousins and M. L. H. Green, *J. Chem. Soc.*, 899 (1963); (e) π-$C_7H_7M(CO)_2C_5H_5$ (M = Mo or W): R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 785 (1964); R. B. King and A. Fronzaglia, *ibid.*, **5**, 1837 (1966); (f) π-$C_6H_5CH_2Mo(CO)_2C_5H_5$: R. B. King and A. Fronzaglia, *J. Am. Chem. Soc.*, **88**, 709 (1966).

[4] Other types of three-electron donor ligands include the following two possibilities: (a) tridentate ligands occupying three coordination positions of the metal atom with donation of one electron through each of these coordination positions of the metal atom and (b) bidentate ligands with three electrons donated through one of the coordination positions and zero electrons donated through the other coordination position.

[5] All of the spectra reported in Table I were recorded on a Beckman IR-9 spectrometer with grating optics and a scale expanded by a factor of 4. At this setting each millimeter of chart paper corresponded to about 1 cm^{-1} below 2000 cm^{-1} and to about 2 cm^{-1} above 2000 cm^{-1}. In order to obtain spectra with a minimum band width,[6] cyclohexane solutions were used in all cases.

[6] For a discussion of the band widths of metal carbonyl bands in various solvents see J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, **4**, 389 (1965).

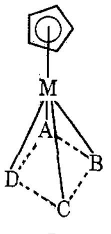
[7] The $C_5H_5M(CO)_2T$ compounds shown to contain bidentate T ligands in this paper could also contain tridentate T ligands.

[8] The alternative possibility of Fermi resonance accounting for the doubling of the carbonyl frequencies appears unlikely since no evidence for it has been noted in any other alkyl or olefin derivatives of metal carbonyls.

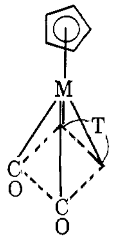
[9] W. Baird and L. F. Dahl, Abstracts of Papers, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept 1963, p 27N.

$C_5H_5Nb(CO)_4$ to have the π-cyclopentadienyl ring on one side of the metal atom and the four carbonyl groups at the corners of a square on the other side of the metal atom. For the $C_5H_5Mo(CO)_2T$ compounds with bidentate T ligands a similar stereochemistry can be considered (structure I), but with the square distorted at least partially to a rhombus with the length of the short diagonal (AC in I) equal to that of a side (*e.g.*, AB in I). With this stereochemistry the bidentate T ligand can occupy either positions A and B leaving positions C and D for the two carbonyl groups (IIa) or positions A and C leaving positions B and D for the carbonyl groups (IIb).[10–12]

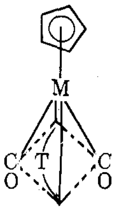
An analogous type of isomerism for $C_5H_5Mo(CO)_2T$ compounds where the T ligand occupies only one coordination position (III) is clearly not possible. Thus solution spectra of compounds III cannot exhibit more than two metal carbonyl stretching frequencies. If four strong metal carbonyl stretching frequencies are observed in a solution spectrum of a $C_5H_5M(CO)_2T$ compound, the T ligand must be occupying two coordination positions. The converse deduction, *i.e.*, the presence of only two strong metal carbonyl stretching frequencies in a solution spectrum indicating the T ligand to occupy only one coordination position, is less reliable, since it is not yet clear either whether both isomers of the type IIa–IIb are actually always present when possible or whether the difference in metal carbonyl stretching frequencies of the two isomers always permits their resolution with available spectrometers.



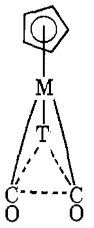
I



IIa



IIb



III

Table I lists the available data on metal carbonyl stretching frequencies of $C_5H_5M(CO)_2T$ (M = Mo or W) compounds all taken under high-resolution conditions.[5] Representatives of the spectra actually obtained are depicted in Figure 1.

These available data show that the compounds $C_5H_5M(CO)_2T$ where the ligand T is a π-allyl or π-cycloheptatrienyl group are the only compounds exhibiting four strong metal carbonyl stretching frequencies and thus the only compounds unequivocally containing a bidentate T ligand. The π-allyl and π-cycloheptatrienyl compounds are likewise the only compounds listed in Table I where three rather than one or two atoms of the T ligand remain continually bonded to the metal atom.[13] The remaining $C_5H_5M(CO)_2T$ compounds (which exhibit only two strong metal carbonyl stretching frequencies) have T ligands bonded to the metal atom either with only one atom (*i.e.*, T = NO or RN_2), with two atoms (*i.e.*, T = CH_3SCH_2), or with a variable number of atoms (*i.e.*, T = π-$C_6H_5CH_2$).

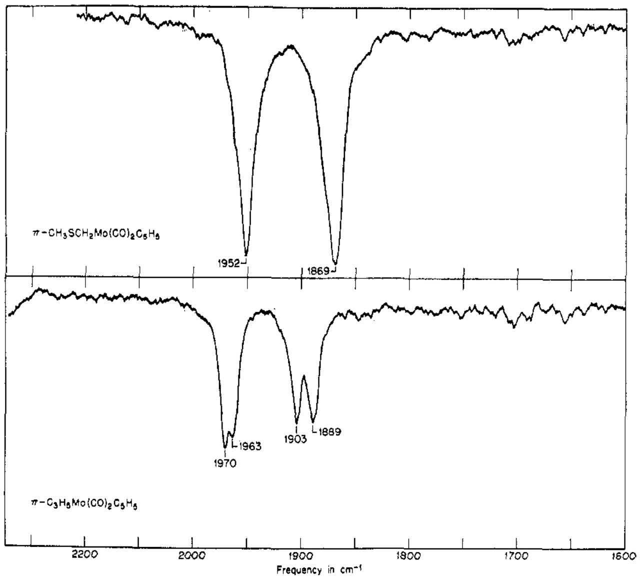


Figure 1.—Typical infrared spectra of $TMo(CO)_2C_2H_5$ compounds.

These data thus suggest that ligands bonded to a metal atom with three atoms occupy two coordination positions ("bidentate") whereas ligands bonded to a metal atom with two or one atoms occupy only one coordination position ("unidentate"). As appropriate compounds become available, further tests will be made both of this general conclusion and of the validity of using the reasoning outlined in this paper for deducing the number of coordination positions occupied by a given ligand.

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[10] On the basis of proton nmr spectral data, positional isomerism similar to that proposed in this paper has been shown to be present in the related $C_5H_5MX_2YZ$ compounds $C_5H_5Mo(CO)_2IP[N(CH_3)_2]_3$[11] and $C_5H_5Mo(NO)I_2P(OC_6H_5)_3$.[12]

[11] R. B. King, *Inorg. Chem.*, **2**, 936 (1963).

[12] R. B. King, *ibid.*, in press.

[13] In the π-benzyl compound π-$C_6H_5CH_2Mo(CO)_2C_5H_5$[3f] the movement of the molybdenum–π-benzyl bond indicated by the temperature dependence of the proton nmr spectrum prevents three carbon atoms of the π-benzyl ligand from remaining *continually* bonded to the molybdenum atom. The proposed "end-run" and "rotation" mechanisms require that only one or two carbon atoms, respectively, of the π-benzyl ligand remain continually bonded to the molybdenum atom.

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RECEIVED JULY 2, 1966