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The Relationship Between π-Cyclopentadienyl Proton N.M.R. Chemical Shifts and Metal Carbonyl Infrared ν(CO) Frequencies in First-Row Transition-Metal π-Cyclopentadienylmetal Carbonyl Derivatives*

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Received November 9, 1968

A least squares linear regression of the πcyclopentadienyl proton n.m.r. chemical shifts versus *the metal carbonyl force constants k_{CO} in 78 cyclopentadienylmetal carbonyl derivatives of the types $C_5H_5Fe(CO)_2X$, $C_5H_5Fe(CO)XL$, $C_5H_5Co(CO)X_2$, $C_5H_5Mn(CO)_2L$, and $C_5H_5Mn(CO)(NO)X$ was performed. The following linear relationship was found:* $\tau(C_5H_5) = 13.203 - 0.499\,k_{CO}$. *The correlation coefficient* (*r*) *was* -0.902. *Many of the compounds which deviated the most from this straight line had the metal atom in a four or five-membered ring also containing a nitrogen, phosphorus, or sulfur atom. The bonding in* π-*cyclopentadienyl derivatives is discussed.*

Introduction

The nature of bonding in metal carbonyl derivatives is most often determined by measurement of the ν(CO) frequencies of the metal carbonyl groups. Changes in the ν(CO) frequencies of metal carbonyl groups have been attributed either to σ-bonding[2,3] or π-bonding effects[4] which have been discussed in detail elsewhere.[5] A recent paper[6] provides a means for distinguishing between the effects of σ-bonding and π-bonding on the ν(CO) frequencies in $YMn(CO)_5$ and $LMo(CO)_5$ molecules.

Readily measured spectroscopic parameters similar to ν(CO) frequencies would be useful for measuring the nature of the bonding of other ligands encountered in coordination chemistry. Of particular interest is the π-cyclopentadienyl ligand in view of the wide variety of stable complexes it forms. A characteristic and readily measured property of the π-cyclopentadienyl ligand in diamagnetic complexes is its single[7] sharp proton n.m.r. resonance. This paper examines the π-cyclopentadienyl n.m.r. chemical shift as an indicator of the nature of the bonding between the π-cyclopentadienyl ring and the metal atom.

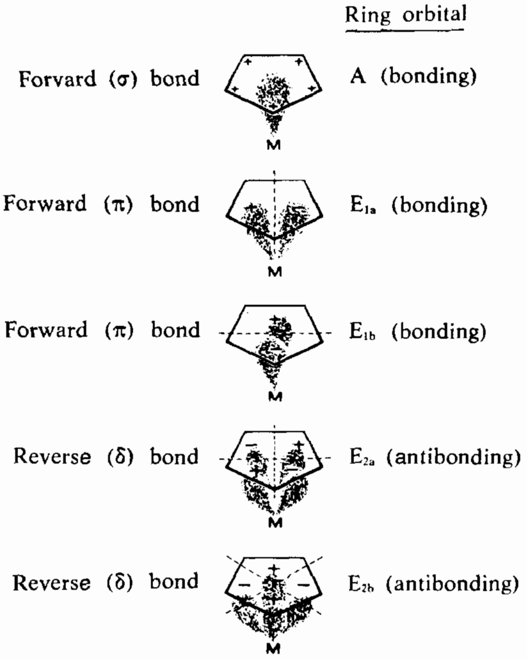

Figure 1. The Components of the Metal-π-cyclopentadienyl Bond.

The π-cyclopentadienyl ring can be considered to form a triple bond with the metal atom (Figure 1). The lowest lying filled A bonding orbital of the π-cyclopentadienyl ring forms a forward σ-bond with an appropriate metal orbital (Table I). The two degenerate filled E_{1a} bonding orbitals of the π-cyclopentadienyl ring form forward orthogonal π-bonds with appropriate metal orbitals (Table I). The resulting metal-π-cyclopentadienyl triple bond contains one σ and two π components like the carbon-carbon triple bond in acetylene.

(*) *Paper presented at the First Inorganica Chimica Acta Symposium Venice, September 1968.*
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(2) R. Poilblanc and M. Bigorgne, *Bull. Soc. Chim. France*, 1301 (1962); M. Bigorgne, *J. Inorg. Nucl. Chem.*, *26*, 107 (1964).
(3) R. J. Angelici, *J. Inorg. Nucl. Chem.*, *28*, 2627 (1966); R. J. Angelici and M. D. Malone, *Inorg. Chem.*, *6*, 1731 (1967).
(4) (a) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, *84*, 4432 (1962); (b) W. D. Horrocks, Jr., and R. C. Taylor, *Inorg. Chem.*, *2*, 723 (1963); (c) F. A. Cotton, *Inorg. Chem.*, *3*, 702 (1964).
(5) G. R. Dobson and L.W. Houk, *Inorg. Chim. Acta*, *1*, 287 (1967).
(6) W. A. G. Graham, *Inorg. Chem.*, *7*, 315 (1968).
(7) In a few tertiary phosphine complexes of cyclopentadienylmetal carbonyls, the π-cyclopentadienyl n.m.r. resonance is split into a doublet or triplet owing to interaction with the spin $\frac{1}{2}$ ^{31}P nucleus. In many π-cyclopentadienylrhodium derivatives the π-cyclopentadienyl n.m.r. resonance is a doublet owing to interaction with the spin $\frac{1}{2}$ ^{103}Rh atom.
(8) The ^{13}C and ^{1}H n.m.r. chemical shifts of the π—C_5H_5 ligands have been shown[9] to possess a linear relationship.

Table I. Metal Orbitals Involved in the Bonding in π-Cyclopentadienylmetal Compounds

Compound Type	Point Group[a]	Example[b]	No. of Forward Bonds			Metal Orbitals Involved in Bonding		
						Forward Bonds		Backward Bonds
			σ	π		σ	π	δ
$C_5H_5MX_4$	C_{4v}	$CpV(CO)_4$	5	2	RF[d]	$2A_1+B_1+E$	E	B_1+B_2
					MO[d,e]	$sp_xp_yp_zd_{x^2-y^2}$	$d_{xz}d_{yz}$	d_{xy}
$C_5H_5MX_3$	$C_{3v}C_{4v}$[f]	$CpMn(CO)_3$	4	2	RF[d]	$2A_1+E$	E	B_1+B_2
					MO[d,e]	$sp_xp_yp_z$	$d_{xz}d_{yz}$	$d_{x^2-y^2}d_{xy}$
$C_5H_5MX_2$	C_{2v}	$CpCo(CO)_2$	3	2	RF[d]	$2A_1+B_1$	B_1+B_2	A_1+A_2
					MO[d,e]	sp_xp_z	d_{xz}(p_y or d_{yz})	$d_{x^2-y^2}d_{xy}$
C_5H_5MX	C_{4v}[g]	CpNiNO	2	2	RF[d]	$2A_1$	E	B_1+B_2
					MO[d,e]	sp_z	p_xp_y	$d_{x^2-y^2}d_{xy}$
$(C_5H_5)_2M$	D_{4h}[g]	Cp_2Fe	2	4	RF[d]	$A_{1g}+A_{2u}$	E_g+E_u	$B_{1g}+B_{2g}+B_{1u}+B_{2u}$
					MO[d,e]	sp_z	$d_{xz}d_{yz}p_xp_y$	$d_{x^2-y^2}d_{xy}$

[a] The π—C_5H_5 ring is treated as a circle rather than a pentagon. [b] Cp=π—C_5H_5. [c] Orbitals required for the forward bonding are assumed to be unavailable for backward bonding regardless of the predictions of group theory. [d] RF=reduced forms of the representations for Γ_σ, Γ_π, and Γ_δ; MO=metal orbitals used in the bonding. [e] This combination is not the only one allowed by group theory. It is selected on the basis of using the s orbital and the three p orbitals for forward bonding. The f orbitals of the heavier metals are not considered. [f] The C_{4v} point group is used to calculate the metal orbitals available for retrodative δ bonding. [g] Because of the fourfold symmetry of the system of π—C_5H_5 E_{1a}, E_{1b}, and E_{2a} orbitals the C_{4v} rather than the $C_{\infty v}$ point group is used for the C_5H_5MX case and the D_{4h} rather than the D_{5h} point group for the $(C_5H_5)_2M$ case.

Besides forming a forward triple bond with a metal atom, the π-cyclopentadienyl ligand can also form a backward (retrodative) bond with the metal atom thus giving the metal-π-cyclopentadienyl bond partial quadruple bond character. The retrodative bond between the metal atom and the π-cyclopentadienyl ring (Figure 1) involves appropriate (Table I) filled *d* orbitals of the metal atom and the empty E_{2a} and E_{2b} antibonding orbitals of the π-cyclopentadienyl ring. This retrodative portion of the metal-π-cyclopentadienyl bond has two nodes and hence may be regarded as a δ bond. The metal-π-cyclopentadienyl bond thus consists of a forward bond with one σ and two π components accompanied by some retrodative δ bonding. This model of the metal-π-cyclopentadienyl bond parallels the generally accepted model[4a] of the metal-carbonyl bond with its forward σ-bond and retrodative π bond.

This model of the metal-π-cyclopentadienyl bond suggests that decreased forward σ- or π-bonding or increased retrodative δ-bonding should increase the electron density on the π-cyclopentadienyl rings raising the shielding and hence the chemical shift of the π—C_5H_5 protons. However, the situations of decreased forward σ- or π-bonding and increased retrodative δ-bonding should both have a tendency to occur in cases where the metal atom has a relatively high negative charge as in anionic derivatives or compounds with many poor retrodative bonding ligands which cannot efficiently remove charge from the metal atom. This reasoning suggests that the proton n.m.r. chemical shift in π-cyclopentadienyl derivatives can be used as a measure of the negative charge on the metal atom with high chemical shifts indicating high negative charges.

In metal carbonyl derivatives a decrease in the carbon-oxygen stretching force constant indicates decreased carbon-oxygen bond order or increased metal-carbon bond order which arises from increased negative charge on the metal atom. The carbon-oxygen stretching force constants can be calculated from the observed infrared ν(CO) stretching frequencies by straightforward techniques. Thus this analysis of the bonding in metal π-cyclopentadienyls and metal carbonyls suggests that increased π—C_5H_5 n.m.r. chemical shifts or decreased carbon-oxygen stretching force constants (*i.e.* decreased ν(CO) frequencies) both should indicate increased negative charge on the metal atom. This further suggests that in metal compounds containing both π-cyclopentadienyl and carbonyl groups the proton n.m.r. chemical shifts and the carbon-oxygen stretching force constants should be related by a monotonic decreasing well-behaved mathematical function. This paper presents data suggesting that this relationship between the proton n.m.r. chemical shifts and the carbon-oxygen force constants in cyclopentadienylmetal carbonyl derivatives of the first-row (3d) transition metals can be approximated by a straight line in the region where actual points occur.[10]

Analysis of the Data

The present study was limited to compounds of the first-row transition metals of the type C_5H_5MXYZ. In order to avoid complications from solvent shifts of the position of the π—C_5H_5 resonance, only n.m.r. spectra taken in $CHCl_3$, $CDCl_3$, CS_2, or CCl_4 were considered. Compounds for which n.m.r. data were only available in solvents such as benzene or acetone were rejected from consideration since test experiments with benzene solutions of compounds such as $Hg[Fe(CO)_2C_5H_5]_2$ and $C_5H_5Fe(CO)_2Mn(CO)_5$ demonstrated that use of benzene rather than CS_2 or $CHCl_3$ as a solvent could often affect the apparent π—C_5H_5 chemical shift by as much as 0.5 p.p.m. This solvent limitation prevented consideration of ionic species in this work.

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(9) P. C. Lauterbur and R. B. King, *J. Am. Chem. Soc.*, 87, 3266 (1965).

(10) It is probable that the actual relationship between $\tau(C_5H_5)$ and k_{CO} is actually a non-linear one but of sufficiently small curvature that a straight line is an adequate approximation in the regions of interest.

(11) For an elementary discussion of the pertinent group theoretical methods see F. A. Cotton, " Chemical Applications of Group Theory ", Interscience, New York (1963).

Table II. $\tau(C_5H_5)$ N.M.R. Chemical Shifts, $\nu(CO)$ Infrared Frequencies, and Force Constants for $C_5H_5Fe(CO)_2X$ Compounds

X	$\tau(C_5H_5)$	$\nu(CO)$ ν_2	ν_1	Mean Value	Force Constants k ($=k_{co}$)	k_i	Reference
C_6H_5CO	5.21	2029	1958	1993	16.03	0.57	a
$C_6H_5CH=CHCO$	5.16	2020	1963	1991	16.01	0.46	a
$CH_2=CHCO$	5.16	2010	1960	1985	15.91	0.40	a
CF_3CO	5.09	2046	1995	2020	16.48	0.42	a
C_2F_5CO	5.03	2048	1998	2023	16.53	0.41	a
C_3F_7CO	5.02	2030	1980	2005	16.23	0.40	a
C_6H_5	5.27	2021	1969	1995	16.07	0.42	a
$CH_2=CH$	5.25	2020	1950	1985	15.91	0.56	a
CF_3	5.06	2053	2003	2028	16.61	0.41	a
C_2F_5	5.01	2054	1999	2026	16.58	0.45	a
$\frac{1}{2}(CF_2)_3$	5.04	2026	1977	2001	16.17	0.40	a
CH_3S	5.11	2032	1985	2008	16.28	0.38	b
$CH_3SCH_2CH_2$	5.31	1990	1930	1960	15.51	0.47	c
CH_3SCH_2	5.21	2000	1940	1970	15.67	0.48	c
CH_3OCO	5.14	2046	1995	2020	16.48	0.42	d
CH_3OCOCH_2	5.20	2030	1979	2005	16.23	0.41	d
$C_2H_5OCOCH_2$	5.24	2016	1963	1990	15.99	0.43	d
CH_3CO	5.13	2035	1969	2002	16.19	0.53	d
Cl	4.96	2050	2010	2030	16.64	0.33	e
C_3H_5	5.45	2010	1948	1979	15.81	0.50	f
C_4H_7	5.44	2016	1950	1983	15.88	0.53	f
$NCCH_2$	5.10	2041	1988	2015	16.40	0.43	g
$NCCH(CH_3)$	5.10	2028	1974	2001	16.17	0.44	g
$NCCH_2CH_2$	5.20	2022	1963	1993	16.04	0.47	g
$\frac{1}{2}Et_2Sn$	5.19	2010	1947	1978	15.80	0.50	h
$C\equiv CCH_3$	5.10	2054	2006	2030	16.64	0.39	i
$n-C_3H_7$	5.41	2013	1953	1983	15.88	0.48	j
$(CH_3)_2CH$	5.42	2012	1953	1983	15.88	0.47	j
CH_2CHO	5.20	2030	1983	2006	16.25	0.38	k
CH_2COCH_3	5.10	2028	1976	2002	16.19	0.42	k
CH_3	5.30	2010	1955	1982	15.86	0.44	l
C_2H_5S	5.16	2028	1983	2005	16.23	0.36	m
C_6H_5S	5.17	2030	1987	2008	16.28	0.35	m
I	4.93	2062	2020	2041	16.82	0.35	n
C_4H_4N	5.07	2020	1975	1997	16.10	0.36	o
H	5.26	2014	1960	1987	15.94	0.43	l
S_2CSCH_3	4.92	2044	2002	2023	16.53	0.34	n
$S_2CSC_2H_5$	4.92	2040	1998	2019	16.46	0.34	n
$S_2CSC_6H_5$	4.96	2048	2001	2024	16.54	0.38	p
CH_3SO_2	4.75	2058	2012	2035	16.72	0.38	n
$C_2H_5SO_2$	4.58	2058	2013	2035	16.72	0.37	p
$C_6H_5SO_2$	4.70	2060	2013	2036	16.74	0.39	p
$C_6H_5CH_2SO_2$	4.90	2060	2010	2035	16.72	0.41	p
$p-CH_3C_6H_4SO_2$	4.91	2060	2012	2036	16.74	0.39	p
$As(CF_3)_2$	5.08	2038	1995	2016	16.41	0.35	q

[a] R. B. King and M. B. Bisnette, *J .Organometal. Chem., 2,* 15 (1964). [b] R. B. King and M. B. Bisnette, *Inorg. Chem., 4* 482 (1965). [c] R. B. King and M. B. Bisnette, *Inorg. Chem., 4,* 486 (1965). [d] R. B. King and M. B. Bisnette, and A. Fronzaglia, *J. Organometal. Chem.,* 5, 341 (1966). [e] T. S. Piper, F. A. Cotton and G. Wilkinson, *J. Inorg. Nucl. Chem., 1,* 165 (1956). [f] M. L. H. Green and P. L. I. Nagy, *J .Chem. Soc.,* 189 (1963). [g] J. K. P. Ariyaratne and M. L. H. Green, *J. Chem. Soc.,* 2976 (1963). [h] F. Bonati and G. Wilkinson, *J. Chem. Soc.,* 179 (1964). [i] J. K. P. Ariyaratne and M. L. H. Green, *J. Organometal. Chem., 1,* 90 (1963). [j] M. L. H. Green and P. L. I. Nagy, *J. Organometal. Chem., 1,* 58 (1963). [k] J. K. P. Ariyaratne and M. L. H. Green, *J. Chem. Soc.,* 1, (1964). [l] A. Davison, J. A. McCleverty, and G. Wilkinson, *J. Chem. Soc.,* 1133 (1963). [m] M. Ahmad, R. Bruce, and G. R. Knox, *J. Organometal. Chem., 6,* 1 (1966). [n] R. Bruce and G. R. Knox, *J. Organometal. Chem., 6,* 67 (1966). [o] P. L. Pauson and A. R. Qazi, *J. Organometal. Chem., 7,* 321 (1967). [p] J. P. Bibler and A. Wojcicki, *J. Am. Chem. Soc., 88,* 4862 (1966). [q] W. R. Cullen and R. G. Hayter, *J. Am. Chem. Soc., 86,* 1030 (1964).

Within these limitations appropriate spectral data for the 78 compounds listed in Tables II thru V were selected for this study. These compounds fell into the five categories $C_5H_5Fe(CO)_2X$, $C_5H_5Fe(CO)XL$, $C_5H_5Co(CO)X_2$, $C_5H_5Mn(CO)_2L$, and $C_5H_5Mn(CO)(NO)X$. Their force constants were obtained from the $\nu(CO)$ frequencies by group theoretical methods[11] similar to those used by Cotton and Kraihanzel[4a] for octahedral metal carbonyl derivatives. The following secular equations were used:

(a) for the dicarbonyls $C_5H_5Fe(CO)_2X$ and $C_5H_5Mn(CO)_2L$:

$$\lambda_2=\mu(k+k_i) \tag{1a}$$

$$\lambda_1=\mu(k-k_i) \tag{1b}$$

(b) for the monocarbonyls $C_5H_5Co(CO)X_2$, $C_5H_5Fe(CO)XL$, and $C_5H_5Mn(CO)(NO)Y$:

$$\lambda=\mu k \tag{2}$$

All of the cases discussed in this paper were very simple ones for the following reasons: (a) sufficient infrared-active frequencies were available for calculations of all of the possible stretching and interaction k_{CO} force constants without any further assumptions;[12] (b) the simultaneous equations were all linear ones simplifying the large number of calculations required

Table III. $\tau(C_5H_5)$ N.M.R. Chemical shifts, $\nu(CO)$ infrared frequencies and force constants for $C_5H_5Fe(CO)LX$ compounds

Compound	$\tau(C_5H_5)$	$\nu(CO)$	Force Constant k_{CO}	Reference
$C_5H_5Fe(CO)(\pi-C_3H_5)$	5.45	1950	15.36	a
$C_5H_5Fe(CO)S_2CSCH_3$	5.41	1965	15.59	b
$C_5H_5Fe(CO)(CH_3)P(C_6H_5)_3$	5.75	1905	14.65	c
$CH_3SCH_2CH_2COFeCOC_5H_5$	5.60	1935	15.12	d
$(CH_3)_2NCH_2CH_2COFeCOC_5H_5$	5.54	1890	14.43	e
$C_5H_5Fe(CO)(COCH_3)P(C_6H_5)_3$	5.38	1920	14.89	f
$C_5H_5Fe(CO)(COCH_3)P(C_4H_9)_3$	5.33	1916	14.82	f
$C_5H_5Fe(CO)(COCH_3)P(OC_6H_5)_3$	5.68	1950	15.35	f
$C_5H_5Fe(CO)(COCH_3)P(OC_4H_9)_3$	5.33	1959	15.50	f
$[C_5H_5Fe(CO)SCH_3]_2$ (stable)	5.75	1952	15.39	g
$[C_5H_5Fe(CO)SC_6H_5]_2$ (stable)	5.51	1978	15.80	g
$[C_5H_5Fe(CO)SCH_3]_2$ (unstable)	5.79	1929	15.03	g
$[C_5H_5Fe(CO)SC_6H_5]_2$ (unstable)	5.97	1938	15.17	g
$[C_5H_5Fe(CO)As(CH_3)_2]_2$ (trans)	5.90	1902	14.61	h
$[C_5H_5Fe(CO)As(CH_3)_2]_2$ (cis)	5.93	1936	15.14	h
$[C_5H_5Fe(CO)P(CH_3)_2]_2$ (trans)	5.84	1902	14.61	h
$[C_5H_5Fe(CO)P(CH_3)_2]_2$ (cis)	5.85	1936	15.14	h
$[C_5H_5Fe(CO)P(C_6H_5)_2]_2$ (trans)	6.13	1917	14.84	h
$[C_5H_5Fe(CO)P(C_6H_5)_2]_2$ (cis)	6.01	1961	15.53	h
$[C_5H_5Fe(CO)As(CF_3)_2]_2$	5.43	1985	15.91	i
$(CF_3CNH)Fe(CO)(NCCF_3)(C_5H_5)$	5.10	1995	16.07	j

[a] M. L. H. Green and P. L. I. Nagy, *J. Chem. Soc.*, 189 (1963). [b] R. Bruce and G. R. Knox, *J. Organometal. Chem.*, *6*, 67 (1966). [c] P. M. Treichel, R. L. Shubkin, K. W. Barnett, and D. Reichard, *Inorg. Chem.*, *5*, 1177 (1966). [d] R. B. King and M. Bisnette, *Inorg. Chem.*, *4*, 486 (1965). [e] R. B. King and M. B. Bisnette, *Inorg. Chem.*, *5*, 293 (1966). [f] J. P. Bibler and A. Wojcicki, *Inorg. Chem.*, *5*, 889 (1966). [g] M. Ahmed, R. Bruce, and G. R. Knox, *J. Organometal Chem.*, *6*, 1 (1966). [h] R. G. Hayter, *J. Am. Chem. Soc.*, *85*, 3120 (1963). [i] W. R. Cullen and R. G. Hayter, *J. Am. Chem. Soc.*, *86*, 1030 (1964). [j] R. B. King and K. H. Pannell, *J. Am. Chem. Soc.*, *90*, 3984 (1968).

Table IV. $\tau(C_5H_5)$ N.M.R. Chemical shifts, $\nu(CO)$ Infrared fre quencies and force constants for $C_5H_5Co(CO)X_2$ Compounds

Compound	$\tau C_5H_5)$	$\nu(CO)$	Force Constant k_{CO}	Reference
$C_5H_5Co(CO)I_2$	4.35	2045	16.89	a
$C_5H_5Co(CO)(CF_3)I$	4.29	2073	17.35	b,c
$C_5H_5Co(CO)(C_2F_5)I$	4.30	2080	17.47	b,c
$C_5H_5Co(CO)(C_3F_7)I$	4.28	2080	17.47	b,c

[a] R. B. King, *Inorg. Chem.*, *5*, 82 (1966). [b] R. B. King, P. M. Treichel, and F. G. A. Stone, *J. Am. Chem. Soc.*, *83*, 3593 (1961). [c] J. A. McCleverty and G. Wilkinson, *J. Chem. Soc.*, 4200 (1964).

Table V. $\tau(C_5H_5)$ N.M.R. Chemical Shifts, $\nu(CO)$ Infrared frequencies, and force constants for Cyclopentadienylmanganese Carbonyl Derivatives.

A. *Compounds of the type $C_5H_5Mn(CO)_2L$:*

L	$\tau(C_5H_5)$	ν_2	$\nu(CO)$ ν_1	Mean Value	$k(=k_{CO})$	References
$CH_2=CHCN$	5.4	1996	1940	1968	15.64	a
$(CH_3)_2PC_6H_5$	5.82	1932	1867	1900	14.58	b
$CH_3P(C_6H_5)_2$	5.91	1935	1872	1903	14.62	b
½ $Me_2PCH_2CH_2PMe_2$	5.83	1931	1866	1899	14.56	b
½ $Ph_2PCH_2CH_2PPh_2$	5.81	1929	1863	1896	14.52	b
½ $Ph_2PCH_2PPh_2$	5.99	1932	1871	1901	14.59	b

B. Compounds of the type $C_5H_5Mn(CO)(NO)X$

X	$\tau(C_5H_5)$	$\nu(CO)$	Force Constant (k_{CO})	Reference
CH_3OCO	4.96	1990	15.99	c
CH_3CO	4.90	2023	16.53	c

[a] M. L. Ziegler and R. K. Sheline, *Inorg. Chem.*, *4*, 1230 (1965). [b] R. G. Hayter and L. F. Williams, *J. Inorg. Nucl. Chem.*, *26*, 1977 (1964). [c] R. B. King, M. B. Bisnette, and A. Fronzaglia, *J. Organometal. Chem.*, *5*, 341 (1966).

for the number of cases considered. In Tables II thru V the $\nu(CO)$ frequencies are given in cm^{-1} and the force constants in mdynes/Å.

Figure 2 depicts a plot of the $\tau(C_5H_5)$ and k_{CO} values for the 78 cases considered. It is immediately apparent that these points approximate a straight line.

In order to explore the linear relationship between $\tau(C_5H_5)$ and k_{CO} in greater detail, a least squares linear regression was run using the IBM 7094 computer at the University of Georgia.

The following equation was obtained:

$$\tau(C_5H_5) = 13.203 - 0.499\ k_{CO} \qquad (3)$$

The correlation coefficient (r) was −0.9026. This straight line is also plotted in Figure 2.

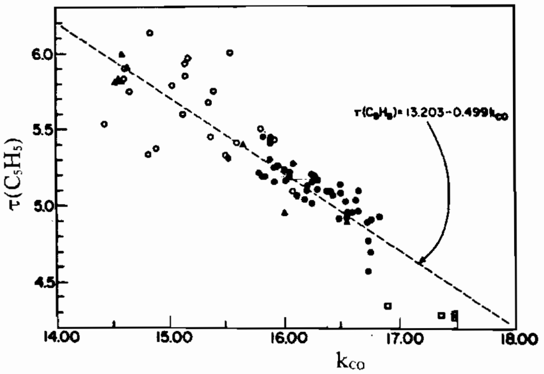

Figure 2. A Plot of $\tau(C_5H_5)$ versus k_{CO} for 78 Cyclopentadienylmetal Carbonyl Derivatives.

Results and Discussion

The high negative correlation coefficient between $\tau(C_5H_5)$ and $\nu(CO)$ indicates that an increase in $\tau(C_5H_5)$ may be used to indicate increased negative charge on the metal atom just like a decrease in the $\nu(CO)$ frequency. This is consistent with the model of the metal-π-cyclopentadienyl bond discussed in the Introduction. This correlation also provides a potentially useful means for studying the bonding in π-cyclopentadienyl derivatives not containing carbonyl groups. Thus compounds of types such as C_5H_5FeQ (Q = five-electron donor ligand such as π-indenyl), $C_5H_5Co(diene)$, or $C_5H_5Fe(diphos)R$ can be investigated in greater detail.

Despite the high negative correlation coefficient between $\tau(C_5H_5)$ and $\nu(CO)$, caution is advised regarding the use of *small* changes in $\tau(C_5H_5)$ as indicators of the negative charge on the metal atom in π-cyclopentadienyl derivatives. The correlation coefficient of ∼−0.9 differs appreciably from the " perfect " value of −1.0. This means that ∼20% of the variation in $\tau(C_5H_5)$ remains unexplained by use of equation (3) in the 78 cases studied. In an attempt to elucidate the causes of some of these discrepancies the actual $\tau(C_5H_5)$ values for the 78 compounds studied were compared with those calculated from the measured k_{CO} by using equation (3). Compounds where the actual values of $\tau(C_5H_5)$ differed from the calculated values by more than ±0.2 p.p.m. are given in Table VI. In many of the compounds listed in Table VI the metal atom is part of a four-membered or, less frequently, a five-membered ring. Constraint of such rings may bend the metal orbitals sufficiently to modify the nature of the metal-π-cyclopentadienyl bond enough to affect the relationship between $\tau(C_5H_5)$ and k_{CO}. Compounds with metal atoms in such rings for which equation (3) is a poor approximation of the relationship between $\tau(C_5H_5)$ and k_{CO} include $(CH_3)_2NCH_2CH_2COFeCOC_5H_5$ and several compounds of the types $[C_5H_5Fe(CO)SR]_2$ and $[C_5H_5Fe(CO)ER_2]_2$ (E = P or As). For the compounds with bridging R_2P and RSgroups the values for $\tau(C_5H_5)$ calculated using equation (3) were consistently too low. Enough of the compounds of the type $C_5H_5Fe(CO)LX$ contain their iron atoms in rings such that a least-squares linear regression analysis of $\tau(C_5H_5)$ *versus* k_{CO} on the 21 compounds of this type listed in Table III yielded a correlation coefficient of −0.430 indicative of a poor correlation for data of this type. A second category of compounds in Table VI exhibiting major discrepancies are some of the cobalt compounds of the type $C_5H_5Co(CO)R_fI$. Hhere the $\tau(C_5H_5)$ and k_{CO} values are both near the extremes of the ranges considered. Possibly the curvature of the actual undetermined relationship between $\tau(C_5H_5)$ and k_{CO} is sufficiently large that the linear equation (3) is no longer a satisfactory approximation at this extreme end.

Table VI. Compounds where the actual and calculated[a] values for $\tau(C_5H_5)$ differ by more than ± 0.2 P.P.M.

Compound	Actual	$\tau(C_5H_5)$ Calcd.[a]	Actual - Calcd.
$[C_5H_5Fe(CO)P(C_6H_5)_2]_2$ cis	6.01	5.45	+0.56
$C_5H_5Fe(CO)(COCH_3)P(C_4H_9)_3$	5.33	5.80	−0.47
$(CH_3)_2NCH_2CH_2COFeCOC_5H_5$	5.54	6.00	−0.46
$C_5H_5Co(CO)I_2$	4.35	4.77	−0.42
$C_5H_5Fe(CO)(COCH_3)P(C_6H_5)_3$	5.38	5.77	−0.39
$[C_5H_5Fe(CO)SC_6H_5]_2$ unstable	5.97	5.63	+0.34
$[C_5H_5Fe(CO)P(C_6H_5)_2]_2$ trans	6.13	5.79	+0.34
$[C_5H_5Fe(CO)As(CH_3)_2]_2$ cis	5.93	5.64	+0.29
$C_2H_5SO_2Fe(CO)_2C_5H_5$	4.58	4.85	−0.27
$CH_3OCOMn(CO)(NO)(C_5H_5)$	4.96	5.22	−0.26
$C_5H_5Co(CO)(CF_3)I$	4.29	4.54	−0.25
$[C_5H_5Fe(CO)SCH_3]_2$ stable	5.75	5.52	+0.23
$[C_5H_5Fe(CO)P(CH_3)_2]_2$ cis	5.85	5.64	+0.21
$CH_3C\equiv CFe(CO)_2C_5H_5$	5.10	4.89	+0.21

[a] Equation (3) was used as a basis for the calculations.

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(12) Compounds of the type $RMo(CO)_3C_5H_5$ are currently being considered. However, this is a much more difficult case since there are four force constants and only three $\nu(CO)$ frequencies. This makes at least one additional assumption necessary.