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ORGANOMETALLIC CHEMISTRY OF THE TRANSITION METALS XIX*. A COMPARATIVE STUDY OF THE TEMPERATURE DEPENDENCE OF THE NMR SPECTRA OF ANALOGOUS CYCLIC POLYOLEFIN COMPLEXES OF CHROMIUM, MOLYBDENUM, AND TUNGSTEN

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INTRODUCTION

Within the last few years, several π-cycloheptatrienyl and π-cyclooctatetraene derivatives of the transition metals have been synthesized. The proton NMR spectra of the π-C_7H_7 or π-C_8H_8 protons in most of these compounds exhibit single fairly sharp resonances at or near room temperature. In some of these compounds such as $C_5H_5CrC_7H_7$ (I), all seven carbon atoms of the π-C_7H_7 group are bonded to the chromium atom[2,3]. The protons are thus equivalent and the observation of a single sharp π-C_7H_7 proton resonance is in accord with expectations. However, in other of these compounds such as $C_5H_5Mo(CO)_2C_7H_7$ (II, M = Mo) only three of the seven carbon atoms of the π-C_7H_7 group are bonded to the molybdenum atom. Since the protons are not formally equivalent, the observation of a single sharp π-C_7H_7 resonance is not in accord with expectations for a static structure such as (II).

In cases such as (II), rapid rotation of the metal around the π-C_nH_n ring ("ring whizzing") was postulated to account for the equivalence of all of the protons in the NMR spectrum. In the cases of $C_8H_8Fe(CO)_3$[4], $C_5H_5Mo(CO)_2C_7H_7$[5], and C_8H_8-$Mo(CO)_3$[6] this postulate now has received strong experimental support from the observation that at low temperatures (−25° to −120°) the resonances due to the π-C_nH_n ($n = 7$ or 8) rings which are singlets at room temperature become markedly broadened or even split into two or more different resonances.

Although the broadening or splitting of π-C_7H_7 or π-C_8H_8 resonances at low temperatures in several compounds is now well established, no comparative studies on closely related series of compounds have been reported. Recent advances in preparative chemistry using $(CH_3CN)_3M(CO)_3$ reagents[7-9] have now made available the previously missing members*** of the two series $C_8H_8M(CO)_3$ (M = Cr[9],

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[*] For Part XVIII see ref. 1.

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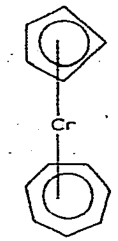
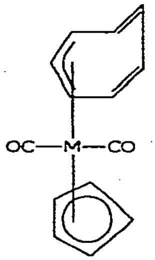
[***] Reactions analogous to those used for the preparation of the molybdenum and tungsten compounds of the type $C_5H_5M(CO)_2C_7H_7$ fail for the preparation for the chromium analogue $C_5H_5Cr(CO)_2C_7H_7$. The difficulty appears to be in the reaction of sodium iodide with the salt $[C_7H_7Cr(CO)_3][BF_4]$ which does not evolve carbon monoxide to yield the required non-ionic iodide $C_7H_7Cr(CO)_2I$. For a detailed discussion of the reactions of the cation $[C_7H_7Cr(CO)_3]^+$ with nucleophiles see ref. 10.



I



II

Mo[6,9], and W[7,8]) and $C_5H_5M(CO)_2C_7H_7$ (M = Mo[2,3] and W[8]). A comparative temperature dependence NMR study on these five compounds is now reported in this paper. This study gives some indication as to the effect of a change in the central metal atom in compounds of otherwise identical types on the temperature dependence of the proton NMR spectrum of the π-C_nH_n ring which in turn provides some clues regarding the relative strengths of the metal–ring bonds.

EXPERIMENTAL

The three cyclooctatetraene complexes $C_8H_8M(CO)_3$ (M = Cr, Mo, and W) were prepared from cyclooctatetraene and the corresponding $(CH_3CN)_3M(CO)_3$ derivatives as described elsewhere[7-9]. The molybdenum complex, $C_8H_8Mo(CO)_3$, possessed a proton NMR spectrum identical to that reported by Winstein, Kaesz, Kreiter, and Friedrich[6] for their $C_8H_8Mo(CO)_3$ compound, obtained from the diglyme complex $(CH_3OCH_2CH_2OCH_2CH_2OCH_3)Mo(CO)_3$ and cyclooctatetraene. The two π-cycloheptatrienyl complexes $C_5H_5M(CO)_2C_7H_7$ (M = Mo and W) were obtained from sodium cyclopentadienide and the corresponding $C_7H_7M(CO)_2I$ compounds[3,8].

The proton NMR spectra in the range −60° to +95° were taken in bromopentafluorobenzene [$C_8H_8M(CO)_3$ compounds] or acetone [$C_5H_5M(CO)_2C_7H_7$ compounds] solutions using a Varian A-60 spectrometer with a variable temperature probe. Attempts to take spectra below −60° of the $C_5H_5M(CO)_2C_7H_7$ compounds were made using a Varian HR-60 spectrometer with a special extremely low temperature probe. However, little additional information was gained, since at these very low temperatures the solubilities were too low* and eventually the solutions froze.

In most cases separations of the resonances could be estimated directly from the chart without any special techniques. In a few cases where broad resonances overlapped, an analogue computer** was used to separate the spectrum into Lorentzian curves of approximate relative intensities corresponding to the number of protons represented.

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* Especially concentrated solutions would be required for observation of the π-C_7H_7 resonances in these solutions at low temperatures since the results described in this paper predict that at these low temperatures the π-C_7H_7 resonances should be so broad that extremely strong spectra would be required for their detection. The π-C_5H_5 resonance, however, could be detected in toluene solutions of $C_5H_5Mo(CO)_2C_7H_7$ at temperatures as low as −100°.

** I am indebted to Dr. E. W. Baker of the Petroleum Fellowship at the Mellon Institute for making available the analogue computer.

DISCUSSION

A. $C_8H_8M(CO)_3$ compounds

In all three cases (M = Cr, Mo, and W) at sufficiently low temperatures spectra could be obtained of $C_8H_8M(CO)_3$ compounds where the uncomplexed olefinic protons (H_d in III) could clearly and widely be separated downfield from the complexed olefinic protons (H_a, H_b, and H_c in III). [See Figs. 1 and 2 for spectra of $C_8H_8M(CO)_3$ (M = Cr and W) compounds at various temperatures.]* At these low temperatures the rotation of the metal–ring bond thus appears to be slowed to a rate negligible relative to the time scale of the NMR measurement. The separation between the three types of complexed protons (H_a, H_b, and H_c in III) is incomplete even at the very low temperatures. However, one type of complexed protons (probably H_c in III) is clearly and widely separated upfield from the other two types of complexed protons in the low-temperature NMR spectra of the three compounds. Thus, for example,

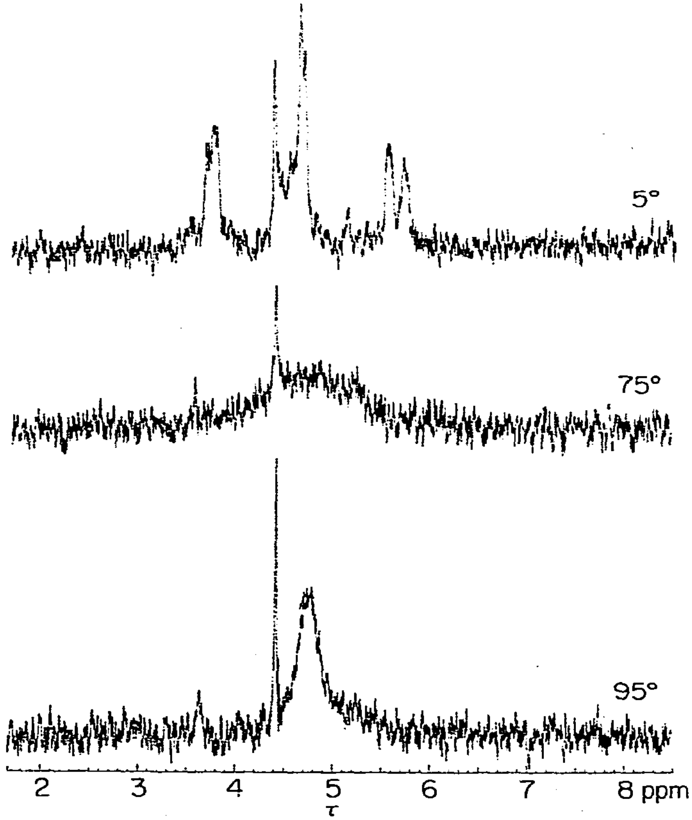

Fig. 1. Temperature dependence of the proton NMR spectrum of $C_8H_8W(CO)_3$.

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* The sharp spike appearing in the range τ 4.3–4.5 in some of the spectra in Figs. 1 and 2 apparently arises from uncomplexed cyclooctatetraene from decomposition.

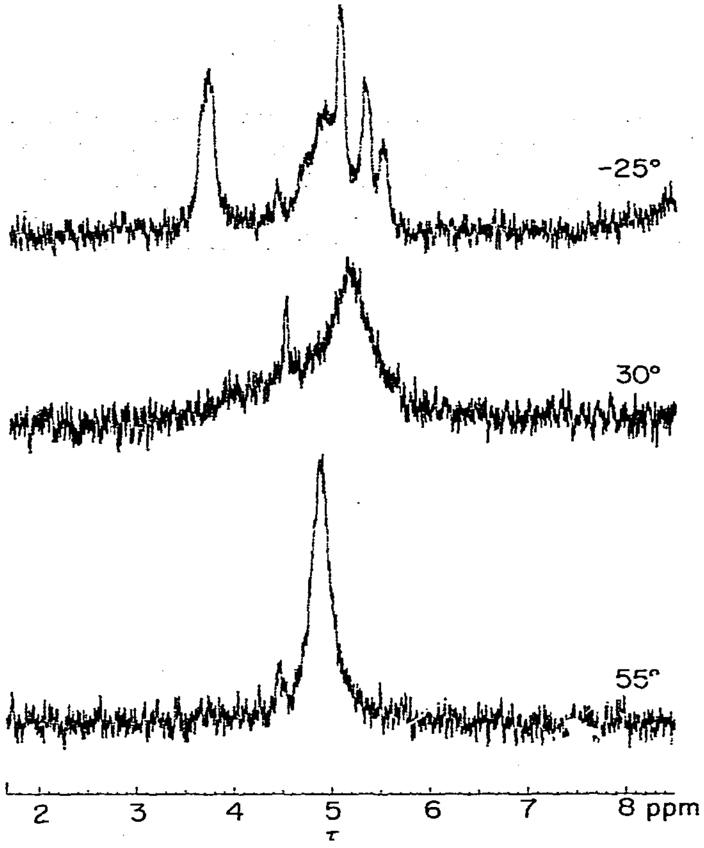
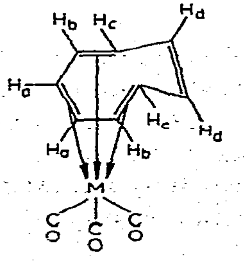


Fig. 2. Temperature dependence of the proton NMR spectrum of $C_8H_8Cr(CO)_3$.

the spectrum of $C_8H_8W(CO)_3$ at 5° (Fig. 1) exhibits resonances at τ 3.76 (broad apparent singlet), τ 4.48 (doublet, $J = 10$ cps), τ 4.68 (apparent singlet), and τ 5.63 (doublet, $J = 10$ cps) of approximate relative intensities 1:1:1:1 which may be assigned (by comparison with the proton NMR spectra of related olefin complexes[11]) to the uncomplexed olefinic protons H_d and the three pairs of complexed olefinic protons H_c, H_a, and H_b, respectively. The 10 cps splitting of the resonances at τ 4.48 and τ 5.63 appears to arise from spin–spin coupling between H_b and H_c.



(III)

Since the NMR spectra of the completely "frozen" forms of the $C_8H_8M(CO)_3$

compounds are available, the technique* developed by Gutowsky and Holm[13] for the quantitative study of hindered internal rotation by nuclear resonance is applicable. The spectra of the $C_8H_8M(CO)_3$ compounds are more complicated than those of the compounds previously used for such studies. This complication and the characteristic-

TABLE 1

DATA USED FOR GUTOWSKY–HOLM CALCULATIONS[a]

Temp. (°C)	$\delta\omega$ (*cps*)	1,000/*T* (°*K*)	$\log_{10}\frac{1}{\tau\delta\omega}$[b]
A. $C_8H_8Cr(CO)_3$			
−25	80[c]	4.03	[d]
−10	79	3.80	−0.96
+ 5	77	3.60	−0.72
+20	72	3.42	−0.51
+30	49	3.30	−0.25
+37	27	3.23	−0.17
+45	18	3.15	−0.16
+55	11	3.05	−0.15
+65	8	2.96	−0.15
+75	6	2.88	−0.15
B. $C_8H_8Mo(CO)_3$			
−30	80[c]	4.12	[d]
−15	78	3.88	−0.80
0	74	3.66	−0.57
+15	69	3.47	−0.44
+30	29	3.30	−0.18
+37	21	3.23	−0.17
+45	13	3.15	−0.16
+55	6	3.05	−0.15
+65	3	2.96	−0.15
+75	2	2.88	−0.15
C. $C_8H_8W(CO)_3$			
−25	56[c]	4.03	[d]
−10	56[c]	3.80	[d]
+ 5	56[c]	3.60	[d]
+20	56[c]	3.42	[d]
+37	54	3.23	−0.72
+45	53	3.15	−0.66
+55	50	3.05	−0.50
+65	49	2.96	−0.47
+75	27	2.88	−0.21
+85	~11	2.79	−0.16

[a] Bromopentafluorobenzene solutions.

[b] $$\frac{1}{\tau\delta\omega} = \sqrt{\frac{1}{2}\left(1 - \frac{\delta\omega^2}{\delta\omega_e^2}\right)}$$

[c] This value was taken as $\delta\omega_e$. [d] Not defined.

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* For an example of the application of this technique to $C_5H_5Rh(C_2H_4)_2$ see ref. 12.

ally large effect of small errors in chemical shift measurements on the calculated activation energies and frequency factors make these values only rough approximations; however, the use of a similar calculation technique for the analogous chromium, molybdenum, and tungsten compounds should at least provide relative information on the strengths of the metal–ring bonds.

With these considerations in mind, the decision was made to use the chemical shift difference between the first resonance due to the uncomplexed olefinic protons (H_d in III) and the third resonance due to two of the complexed olefinic protons (H_a in III) as the basis for the Gutowsky-Holm calculations in the $C_8H_8M(CO)_3$ compounds. This chemical shift difference appeared to be the most easily measured of the various possible chemical shift differences. It also appeared relevant to the question of rotation of the C_8H_8 ring.

The data used for the Gutowsky–Holm calculation are given in Table 1. Routine least-squares linear regression analysis was used to generate the "best" straight lines from the available points. Correlation coefficients (r) were at least 0.97 and generally 0.99 or better. The resulting plot of $\log_{10}[1/(\tau\delta\omega)]$ *versus* $1/T$ is given in Fig. 3. The activation energies (E_a) and frequency factors (ν_0) corresponding to the rate equation $k = \nu_0 \exp(-E_a/RT)$ calculated from these data are given in Table 2.

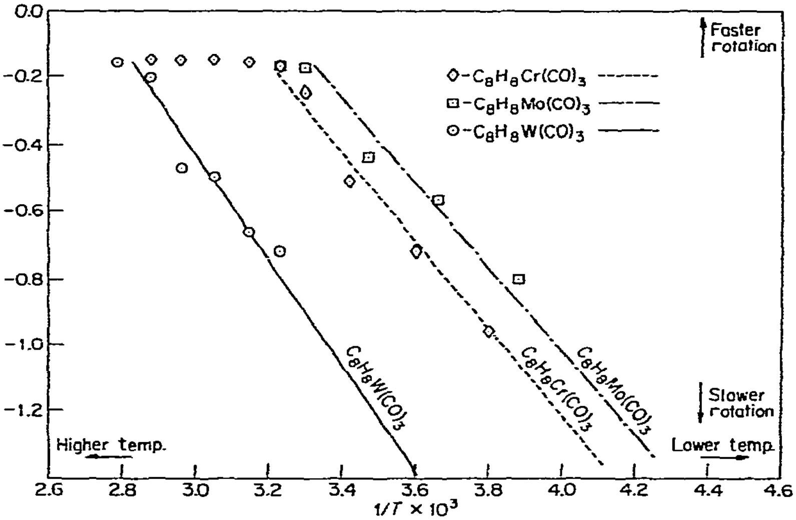

Fig. 3. $\mathrm{Log}_{10}(1/\tau\delta\omega)$ *vs.* $1/T$ for $C_8H_8M(CO)_3$ compounds.

TABLE 2

ACTIVATION ENERGIES AND FREQUENCY FACTORS FOR TRANSITION METAL COMPLEXES

	Compound	*Solvent*	E_a *(cal)*	ν_0 *(sec.*$^{-1}$ $\times 10^5$)
1)	$C_8H_8Cr(CO)_3$	C_6F_5Br	6000	4.6
2)	$C_8H_8Mo(CO)_3$	C_6F_5Br	5800	4.5
3)	$C_8H_8W(CO)_3$	C_6F_5Br	7200	16.1
4)	π-$C_6H_5CH_2Mo(CO)_2C_5H_5$[a]	C_6F_5Br	6100	5.5
5)	$C_5H_5Rh(C_2H_4)_2$[b]	$CHCl_3$	6200	6.6

[a] Obtained from data from ref. 5. [b] Data from ref. 12.

The values for the $C_8H_8M(CO)_3$ compounds thus obtained are similar to those previously obtained for the complexes π-$C_6H_5CH_2Mo(CO)_2C_5H_5$ and $C_5H_5Rh(C_2H_4)_2$ where a system of a metal and a π-bonded ligand are also involved in rotation or other types of motion.

The results summarized in Table 2 thus indicate that the rate of rotation decreases in the series $C_8H_8Mo(CO)_3$ (fastest) $> C_8H_8Cr(CO)_3 \gg C_8H_8W(CO)_3$ (slowest). This parallels the reactivity of the corresponding hexacarbonyls since hexacarbonylmolybdenum is the most reactive and hexacarbonyltungsten the least reactive[14,*]. Presently available data suggest that at least in hexacoordinate compounds with the favored rare gas configuration the stability of metal–carbon bonds increases in the order Mo–C (least stable $<$ Cr–C $\ll$ W–C (most stable). This suggests that when a reactive organometallic compound is desired, the molybdenum derivative should be used and when a stable organometallic compound is desired the tungsten derivative should be used. The much greater stability of the metal–ring bond in $C_8H_8W(CO)_3$ as compared with its chromium and molybdenum analogues found from this NMR study is consistent with the apparently greater oxidative and thermal stability of $C_8H_8W(CO)_3$ relative to its chromium and molybdenum analogues[7–9].

B. $C_5H_5M(CO)_2C_7H_7$ compounds

A detailed treatment of the compounds $C_5H_5M(CO)_2C_7H_7$ (M = Mo and W) by the Gutowsky–Holm technique[13] was not possible because NMR spectra could not be obtained at sufficiently low temperatures for the various types of π-C_7H_7 protons to be completely separated.

Nevertheless, it is quite apparent that the π-C_7H_7 proton resonance of the $C_5H_5M(CO)_2C_7H_7$ compounds becomes broader relative to the π-C_5H_5 resonance as the temperature is lowered[5]. The ratio W_7/W_5 where W_7 is the width at half-height of the π-C_7H_7 resonance and W_5 is the width at half-height of the π-C_5H_5 resonance provides a measure of the broadening of the π-C_7H_7 resonance which is independent of spectrometer performance or other factors which would also affect the width of the π-C_5H_5 resonance. Table 3 gives the values for W_7/W_5 found for the $C_5H_5M(CO)_2C_7H_7$ (M = Mo or W) compounds at various temperatures.

The limiting value of the ratio W_7/W_5 (designated as W_7^0/W_5^0) as the temperature is raised represents the value for freely rotating rings. Increases in W_7/W_5 above this limiting value W_7^0/W_5^0 provide a measure of the slowing down of the rotation as the temperature is reduced. Fig. 4 depicts for $C_5H_5M(CO)_2C_7H_7$ (M = Mo and W) plots of $\log_{10}(W_7/W_5 - W_7^0/W_5^0)$ *versus* the reciprocal of the absolute temperature which approximate straight lines (least-squares correlation coefficients $r > 0.99$).

The data presented in Table 3 and Fig. 4 indicates that the rate of rotation of the π-C_7H_7 ring for $C_5H_5Mo(CO)_2C_7H_7$ is greater than that for $C_5H_5W(CO)_2C_7H_7$.

This corresponds entirely to the relative rates of rotation of the corresponding

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[*] For a study of the comparative ease of displacement of one carbonyl group from compounds of the type (bipy)$M(CO)_4$(M = Cr, Mo, or W) bipy = 2,2'-bipyridine with phosphites to form compounds of the type *cis*-(bipy)$M(CO)_3P(OR)_3$ see ref. 15. With the chromium compound (bipy)$Cr(CO)_4$ the displacement reaction was found to proceed according to a first-order rate law. However, with the molybdenum and tungsten compounds (bipy)$M(CO)_4$ (M = Mo and W), the rate law of the displacement reaction was found to contain both a first-order and a second-order term.

TABLE 3

RESONANCE WIDTHS IN $C_5H_5M(CO)_2C_7H_7$ COMPLEXES[a]

Temp. (°C)	W_5 (*cps*)	W_7 (*cps*)	1000/*T* (°K)	$log_{10}(W_7/W_5 - W_7^0/W_5^0)$
A. $C_5H_5Mo(CO)_2C_7H_7$				
−60	1.8	19.5	4.70	+1.04
−45	1.5	10.1	4.38	+0.76
−30	1.9	3.9	4.12	+0.04
−15	1.5	2.4	3.88	−0.15
0	1.4	1.7	3.66	−0.52
+15	1.5	1.5	3.47	−1.00
+30[b]	2.8	2.5	3.30	[c]
B. $C_5H_5W(CO)_2C_7H_7$				
−45	1.9	28	4.38	+1.15
−30	1.9	14.5	4.12	+0.85
−15	1.9	6.2	3.88	+0.43
0	1.5	2.8	3.66	+0.11
+15[b]	2.9	1.9	3.47	[c]
+30	3.8	2.4	3.30	[c]

[a] Acetone solutions. [b] Values at this temperature were taken as W_5^0 and W_7^0. [c] Not defined.

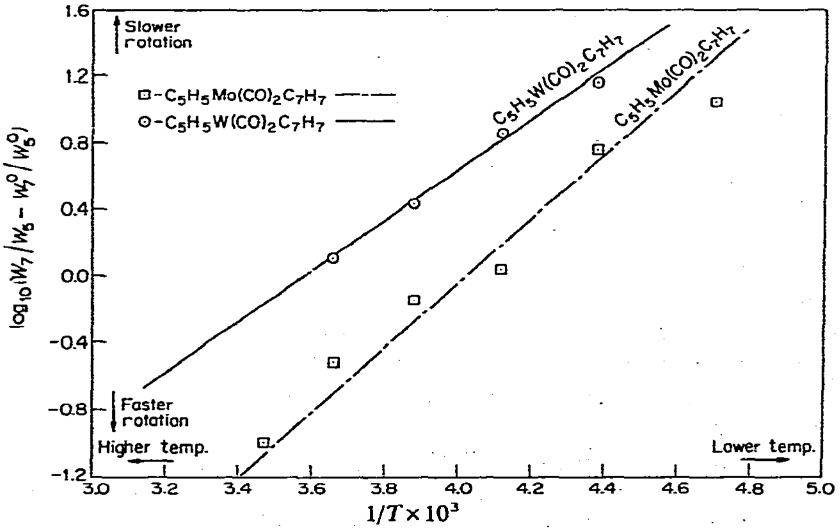

Fig. 4. $Log_{10}(W_7/W_5 - W_7^0/W_5^0)$ *vs.* $1/T$ for $C_5H_5M(CO)_2C_7H_7$ compounds.

$C_8H_8M(CO)_3$ complexes discussed above and provides further support for the greater strength of tungsten–carbon bonds relative to molybdenum–carbon bonds.

SUMMARY

The temperature dependence of the proton NMR spectra of the compounds $C_8H_8M(CO)_3$ (M = Cr, Mo, and W) and the compounds $C_5H_5M(CO)_2C_7H_7$ (M = Mo or W) is discussed. Evidence is presented to indicate that the rate of rotation of

the metal atom around the π-C_nH_n ring decreases in the series molybdenum (fastest) > chromium ≫ tungsten (slowest).

REFERENCES

1 R. B. King, *Inorg. Chem.*, 6 (1967) 30.
2 E. O. Fischer and S. Breitschaft, *Angew. Chem.*, 75 (1963) 94.
3 R. B. King and M. B. Bisnette, *Inorg. Chem.*, 3 (1964) 785.
4 F. A. Cotton and R. Pettit, *Ninth Robert A. Welch Foundation Conference on Chemical Research*, Houston, Texas, November, 1965.
5 R. B. King and A. Fronzaglia, *J. Am. Chem. Soc.*, 88 (1966) 709.
6 S. Winstein, H. D. Kaesz, C. G. Kreiter and E. C. Friedrich, *J. Am. Chem. Soc.*, 87 (1965) 3267.
7 R. B. King and A. Fronzaglia, *Chem. Commun.*, (1965) 547.
8 R. B. King and A. Fronzaglia, *Inorg. Chem.*, 5 (1966) 1837.
9 R. B. King, *J. Organometal. Chem.*, 8 (1967) 161.
10 J. D. Munro and P. L. Pauson, *J. Chem. Soc.*, (1961) 3475.
11 M. A. Bennett, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, (1961) 2037.
12 R. D. Cramer, *J. Am. Chem. Soc.*, 86 (1964) 217.
13 H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, 25 (1956) 1228.
14 R. B. King, Ph. D. Dissertation, Harvard University, 1960; R. B. King and F. G. A. Stone, *J. Am. Chem. Soc.*, 83 (1961) 3590.
15 R. J. Angelici and J. R. Graham, *J. Am. Chem. Soc.*, 87 (1965) 5586; J. R. Graham and R. J. Angelici, *J. Am. Chem. Soc.*, 87 (1965) 5590.