Journal of Organometallic Chemistry, 77 (1974) 1—25
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Review

CARBON-13 NUCLEAR MAGNETIC RESONANCE SPECTRA OF METAL CARBONYL COMPOUNDS

LEE J. TODD and JOHN R. WILKINSON
Department of Chemistry, Indiana University, Bloomington, Indiana 47401 (U.S.A.)

(Received March 4th, 1974)

Contents

I. Introduction

One of the major difficulties in the study of metal carbonyl compounds has been structure elucidation. In many cases the infrared spectrum of a new metal carbonyl derivative at best could only indicate the presence of terminal and/or bridging carbonyl groups. Generally researchers relied upon a time consuming single crystal X-ray structure determination for definite structural information. With the advent of pulsed Fourier transform NMR equipment, rapid advances in the application of ^{13}C NMR spectra for the determination of metal carbonyl structures have been made. In addition, by variation of temperature, this powerful new technique has allowed detailed study of the fluxional nature of certain metal carbonyl systems, particularly those which do not have proton-containing ligands.

Although short discussions of "the ^{13}C NMR spectra of organometallic compounds" have appeared previously [1,62] no detailed treatment concerning ^{13}C NMR studies of metal carbonyl compounds per se has appeared. We outline in this review the majority of reported ^{13}C NMR data of transition metal carbonyl compounds through 1973. The various carbonyl carbon shielding trends are discussed in detail. These trends have thus far proven to be very consistent and errors in the literature are easily spotted. In certain cases these errors have been corrected by direct personal communication with the authors.

Several troublesome technical problems in the measurement of metal carbonyl ^{13}C NMR spectra have been encountered such as (1) the slow relaxation times of carbonyl carbon nuclei, (2) the low solubility of some complexes of interest and (3) the quadrupole broadening effects to the carbonyl resonances caused by certain transition metals (e.g. ^{55}Mn and ^{59}Co). The progress that has been made to overcome these problems will also be reviewed.

II. Methodology for obtaining the ^{13}C NMR spectra of metal carbonyls

^{13}C NMR has proved to be a powerful new tool for the study of organometallic compounds. As the technical problems are being overcome the number of reports of the use of this technique for molecular structure elucidation are increasing rapidly. This section is included as an introduction to some experimental problems encountered in obtaining ^{13}C NMR spectra of metal carbonyl complexes and suggested solutions to the problems.

Metal-bonded carbonyl carbons have unusually long T_1 relaxation times. This property in many cases partially undermines the advantages of Fourier transform methods because long recycle times are required between successive pulses. Recently a shiftless relaxation reagent, $Cr(acac)_3$, has been reported [36] which circumvents this problem and permits pulse intervals of 0.5-2 sec. This reagent is kinetically inert and soluble in many organic solvents. No contact shift has been observed at higher concentrations with the use of this reagent. Higher concentrations of $Cr(acac)_3$ do cause some line broadening. In our ^{13}C NMR measurements we generally use $0.07M$ concentrations of the reagent.

Another problem encountered in obtaining ^{13}C NMR spectra of metal carbonyl derivatives is that many compounds, particularly polynuclear carbonyls, have relatively limited solubilities. This difficulty can be overcome by enriching the carbonyl compound via intermolecular exchange with ^{13}CO. There are several literature sources which deal in part with the kinetics and mechanisms of CO exchange with metal carbonyls [2-8]. However, none of these reviews are very useful in a practical sense when one is confronted with the ^{13}CO enrichment of a new metal carbonyl compound. The first and simplest approach is to stir a sample of the compound in an appropriate solvent under a static atmosphere of ^{13}CO until equilibrium is reached. The choice of solvent can be important and in certain cases an increase in exchange rate has been observed with an increase in the solvent donor ability [9]. Ether solvents are particularly useful in this respect and in addition CO has a relatively high solubility in these solvents. This approach is most useful with metal carbonyl compounds which undergo CO exchange fairly easily. In general this includes molecules which are coordinatively unsaturated, which have bridging carbonyl groups, or compounds containing "hard bases" as ligands. More drastic means which can be used to cause CO exchange are (a) thermal treatment, (b) photochemical treatment [63] and (c) the use of catalytic agents. Catalysts mentioned in the literature are palladium supported on carbon [50] and acids such as trifluoroacetic acid [2,50]. The

TABLE 1
CHEMICAL SHIFT VALUES FOR REFERENCE MATERIALS AND SOLVENTS

Compound	δ(C) (ppm)[a]
CS_2	192.4
Chloroform	77.2
Methylene chloride	53.9
Benzene	128.6
Tetrahydrofuran	26.3 68.0
Acetone	30.4 205.1

[a] TMS = 0 ppm.

choice of these more drastic methods depends upon the lability of the particular compound in question.

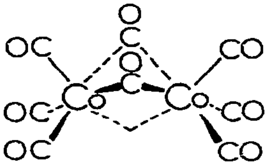
The most generally used reference compound at present is tetramethylsilane (TMS). In this review individual carbonyl shieldings (δ(C) are expressed in parts per million (ppm) relative to TMS. Positive δ(C) values are at lower field than TMS. In practice the solvent used in the ^{13}C NMR experiment is often also employed as a secondary reference. This mode of operation assumes that the solvent shielding is concentration and temperature independent. In earlier work other compounds such as carbon disulfide and benzene were used as reference materials. In Table 1 are given the δ(C) values for reference materials and solvents which will be used in this review.

Many of the earlier data were obtained with continuous wave instruments and the limit of error is ± 0.3 ppm at best. With Fourier transform instruments errors of ± 0.1 ppm or less can generally be obtained. Considering these errors as well as the errors which inevitably occur when one collects together data from many different laboratories, δ(C) values will be listed only to one significant figure beyond the decimal point.

There are a number of general references concerning pulsed Fourier transform methods and their specific application to ^{13}C NMR which we have found useful for many specific problems [1,62,84] and they are included here for the reader's convenience.

III. Metal carbonyls without other ligands

Iron pentacarbonyl was one of the first molecules of this class to be studied by ^{13}C NMR [11]. Electron diffraction studies reveal a trigonal bipyramidal structure for this molecule. For this structure two ^{13}C resonances would be anticipated. To date only one resonance has been observed for this molecule. Iron contains 2.19% of ^{57}Fe ($I = \frac{1}{2}$) and $^{1}J(^{57}\text{Fe}—^{13}\text{C}) = 23.4$ Hz has been observed for $Fe(CO)_5$ [13]. This information indicates that there is no intermolecular exchange of carbonyl ligands. The possiblities that still must be considered are (a) rapid intramolecular interchange or (b) an unresolvable difference in shielding of the two types of terminal carbonyl ligands. Attempts to slow down the expected intramolecular site exchange of $Fe(CO)_5$ at —63, —110, and —170°C have failed to resolve the carbonyl peak into two signals [12,88,14,16].



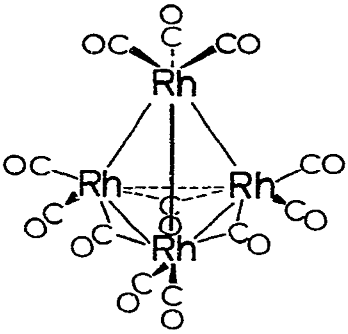


Fig. 1. The solid state structure of $Co_2(CO)_8$.

Fig. 2. The solid state structure of $Rh_4(CO)_{12}$.

The ^{13}C NMR of $Mn_2(CO)_{10}$ has been difficult to obtain due to quadrupolar broadening effects [$^{55}Mn(I = 5/2)$, 100% natural abundance]. However with a ^{13}C-enriched sample two broad signals at 223 and 212.9 ppm were obtained [55].

In the solid state [85] it has been established that $Co_2(CO)_8$ has a bridge carbonyl structure (Fig. 1), while from infrared studies [86] in solution this form is in equilibrium with the all-terminal carbonyl isomer. The ^{13}C NMR spectrum of $Co_2(CO)_8$ even at —90°C contains only one signal at 203.8 ppm in the terminal carbonyl region [55]. It is suspected that this molecule is undergoing intramolecular site exchange. Thus the observed signal is probably a weighted average of a terminal resonance which would be at slightly higher field (from 6 carbonyl groups) and a bridge resonance at much lower field (from 2 carbonyl groups). It is obvious that a ^{13}C NMR spectrum at a temperature well below —100°C will be needed to obtain a static structure.

While both $Fe(CO)_5$ and $Fe_3(CO)_{12}$ appear to be fluxional at room temperature since each molecule exhibits only one carbonyl resonance, the ^{13}C NMR spectrum of $Ru_3(CO)_{12}$, obtained with a ^{13}CO-enriched sample contained two resonances of nearly equal area,[55] which can be assigned to the equal number of axial and equatorial terminal carbonyl groups of a static structure as found in the X-ray crystal study of this molecule [87].

The ^{13}C NMR spectrum of ^{13}C-enriched $Rh_4(CO)_{12}$ at room temperature consists of a broad featureless peak [18]. At +63° the spectrum was resolved into a 1/4/6/4/1 quintet with a splitting of 17.1 Hz. The limiting low temperature spectrum was obtained at —65°, exhibiting four multiplets of equal intensity [69]. There was a triplet at 228.8 (bridging carbonyls) and three doublets at 183.4, 181.8 and 175.5 ppm. The spectrum is compatible with the four types of carbonyl groups observed for this compound in the solid state (Fig. 2). The doublet at 183.4 ppm has the narrowest line width and was assigned to the apical carbonyl groups on the basis that these carbon nuclei would participate in the simplest local spin system.

The ^{13}C NMR spectra of metal carbonyl anions have not been investigated to any large extent thus far. The presently available data indicates that within an isoelectronic series, shieldings of the anion carbonyls are found consider-

TABLE 2

^{13}C NMR SHIELDINGS OF THE ACYL CARBON OF $Z^+[(CO)_4Fe\overset{\overset{O}{\|}}{C}H]$ — printed with the O set below the C: $Z^+[(CO)_4Fe\underset{\underset{O}{\|}}{C}H]$

Solvent	Z^+	δ(C) (acyl carbon)
THF	Na^+	275.8
THF—HMPA	Na^+	257.6
THF	$N(PPh_3)_2{}^+$	260.1

ably down field of the neutral carbonyls. This is seen with the following isoelectronic molecules: $[V(CO_6][Na(diglyme)_2]$ [15] and $Cr(CO)_6$ with shieldings of 225.7 and 212 ppm respectively; $[Ph_3P{=}N{=}PPh_3][Co(CO)_4]$ [55] and $Ni(CO)_4$ with shieldings of 211.2 and 191.6 ppm respectively. A recent study of the ^{13}C NMR spectrum of the $[(CO)_4Fe\overset{\overset{O}{\|}}{C}H]^-$ ion contains a very important caveat [21]. The spectrum of the anion is markedly dependent on the nature of the cation and its state of solvation. The ^{13}C NMR data in Table 2 illustrates this point. In the presence of strongly coordinating solvents such as hexamethylphosphoramide (HMPA), the sodium ion is tied up and functions like the

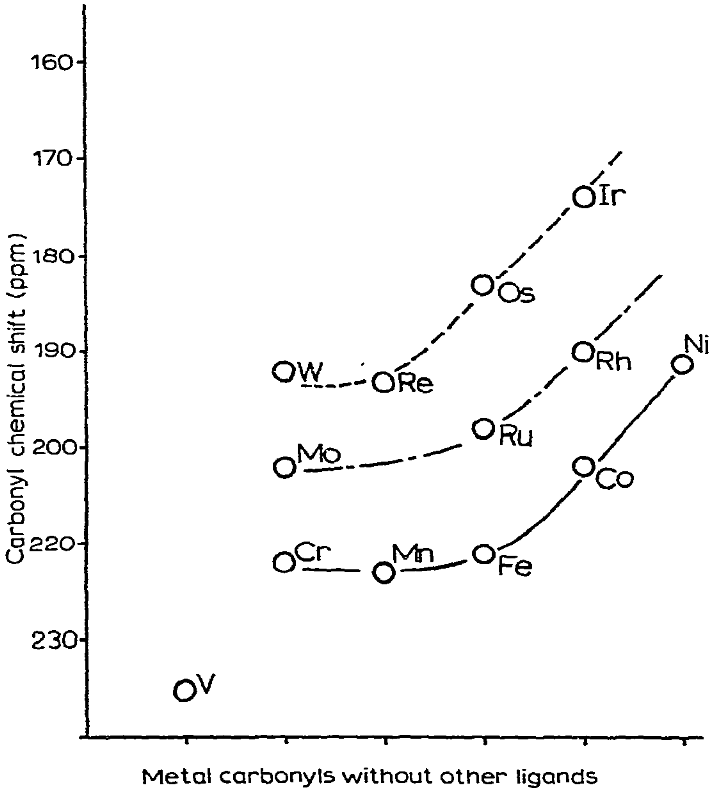


Fig. 3. The chemical shift trend of the terminal resonances for the parent metal carbonyl derivatives.

$N(PPh_3)_2^+$ ion. However in THF solvent alone a tight ion pair, $Na^+ \cdots [O{=}\overset{H}{C}Fe(CO)_4]^-$ is formed which significantly deshields the acyl carbon atom.

The chemical shift trend of terminal carbonyl resonances for the parent metal carbonyl compounds is presented in Fig. 3. In certain cases (Ir and Os) values for the parent carbonyls are not presently available and a value of a substitute derivative was used. Fortunately in these particular cases rather narrow chemical shift ranges are anticipated. The $\delta(C)$ value for vanadium was that of $V(CO)_6$ We would anticipate a more shielded value for a "neutral" vanadium carbonyl. A marked increase in shielding is observed for the heavier metal carbonyls of each period. We interpret this as being due to a gradual increase in donor/acceptor ratio (decreased π-back bonding) as one progresses from left to right within a given period. This may be caused by the increased effective nuclear charge experienced by the metal *d* electrons from left to right within a period which decreases the extent of π-back bonding.

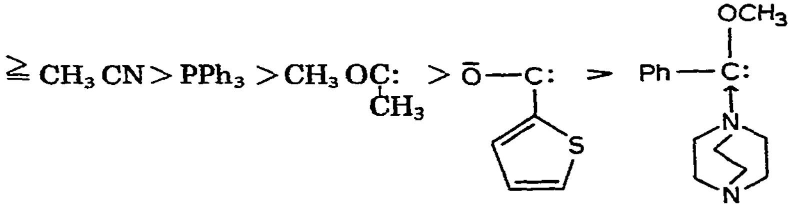
Another trend observed in Fig. 3 is the increase in carbonyl shielding as one progresses down a given group in the periodic table. This is most clearly seen in Group VIB. The carbonyl shieldings of $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$ are 212, 202 and 192 ppm respectively [17,20]. The same trend is apparent, although somewhat less clearcut, in the other groups. The ambiguity is due to the rather large changes in structure and degree of aggregation of the other transition metal carbonyls.

IV. Metal carbonyls containing other ligands

A. Chromium, molybdenum and tungsten carbonyl derivatives

Substituted metal carbonyl compounds of these metals have been the most extensively studied thus far via ^{13}C NMR. This is due to the relative ease with which they can be prepared, their ^{13}C NMR measured, and the results interpreted. In a study of the complexes of the general formula $LW(CO)_5$ [$L = P(OC_6H_5)_3$, $P(O\text{-}n\text{-}C_4H_9)_3$, $P(C_6H_5)_3$, $As(C_6H_5)_3$, $Sb(C_6H_5)_3$, $NH_2(C_6H_{11})$ and others], a linear correlation was found to exist between the Cotton—Kraihanzel derived carbonyl stretching force constants and the corresponding carbonyl carbon shieldings [17]. The most shielded carbonyl has the largest force constant. This same type of linear relationship has been observed for changes of L with a given metal in several other classes of complexes [i.e. $LCr(CO)_5$, $LMo(CO)_5$ and $L(CO)_2Fe(\pi\text{-}C_5H_5)$] [20,23,38]. These relationships suggest that changes in the interaction of metal *d*-orbitals with carbonyl π^* orbitals strongly influence carbonyl carbon shielding.

Several trends can be seen in the carbonyl carbon shielding data (see Section V). (Trend 1) The carbonyl resonances of a substituted complex are at lower field than the carbonyl shielding of the parent metal hexacarbonyl. This trend has been interpreted as being due to the relatively high value of the σ-donor/π-acceptor ratio of most ligands compared with CO [22]. (Trend 2) The carbonyl *trans* to a substituent L is more deshielded than the carbonyls that are *cis*. This suggests that the *trans* carbonyl obtains metal *d*-orbital electron density (via π-back bonding) more readily than most substituent ligands. Comparison of the *trans* carbonyl ^{13}C chemical shifts of a series of $LCr(CO)_5$ derivatives shows the following order of decreased shielding: L = $CO > P(OPh)_3 > CH_3C_6H_4NC$



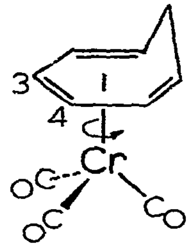
It is suggested that this is also the order of increasing σ-donor/π-acceptor ratio of these ligands. Thus the ylide ligand at the far right of the series is a good donor but a poor acceptor. The order of decreased shielding is the same for $LW(CO)_5$ derivatives also. (Trend 3) Successive replacement of CO by other ligands results in the remaining carbonyl resonances being situated at even lower field. A good example of this trend is seen in the series $(C_2H_5)_3PW(CO)_5$, *trans*-$[(C_2H_5)_3P]_2W(CO)_4$ and *fac*-$[(C_2H_5)_3P]_3W(CO)_3$ which have the shieldings 200.2 *(trans)*, 198.5 *(cis)*; 204.7; and 212.4 ppm respectively [20,71]. (Trend 4) Changing the metal from Cr to Mo and Mo to W maintaining the same array of ligands results in an upfield shift of the carbonyl shieldings of about 10 ppm for each change. This is the same trend noted earlier for the parent metal carbonyls.

Finer details of carbonyl shielding trends are observed in $\left(\begin{smallmatrix}R\\R'\end{smallmatrix}\!>\!C\right)M(CO)_5$ derivatives for which a large number (approximately 50 compounds) have been reported.

Substitution of an amino group for the methoxy group in $\begin{smallmatrix}CH_3O\\CH_3\end{smallmatrix}\!>\!C{=}Cr(CO)_5$ appears to make the carbene ligand a better electron donor. This results in a downfield shift of the carbonyl resonances in the amino derivative. Although the change is small due to the remoteness of the substituent from the carbonyl carbons, the same trend is observed in several cases. Most interesting is the fact that the *cis*-carbonyl resonance moves downfield to a larger extent than the *trans* shielding. This can be rationalized by assuming that π-back bonding to the *trans* carbonyl has approached the "saturation point" in the carbene complex and that additional electron density donated to the metal (in the case of the amino carbene derivative) is transmitted preferentially to the *cis* carbonyls via π-back donation.

The shielding of a variety of (π-arene)$M(CO)_3$ derivatives have been reported [15]. Within the limits of the data, the π-arene group appears to have nearly the same shielding effect as three monodentate R_3P ligands in a *fac*-$L_3M(CO)_3$ derivative. For example, one can compare the shieldings of π-mesitylene tricarbonyltungsten and *fac*-$[(C_2H_5)_3P]_3W(CO)_3$ which have the values 212.6 and 212.4 ppm respectively. Comparison of the carbonyl shieldings of a series of $(\pi\text{-}C_6H_5X)Cr(CO)_3$ derivatives [15] indicates that deshielding increases as the electron donating ability of the X substituent increases. This is the same relationship observed earlier in this section for $LM(CO)_5$ derivatives.

At room temperature the triene ligands of both tricarbonyl-1,3,5-cycloheptatrienechromium(0) and the corresponding molybdenum(0) complex ap-



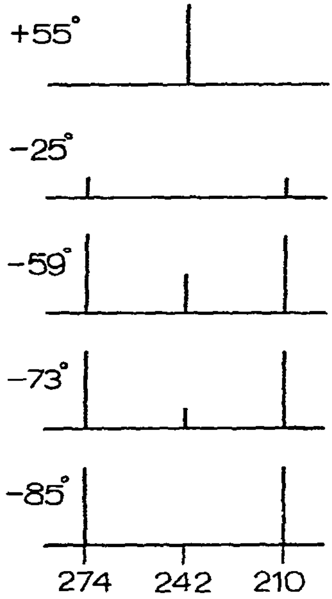
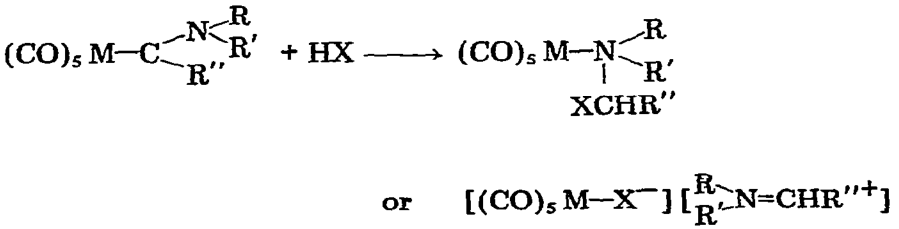


Fig. 4. A structure of tricarbonyl-1,3,5-cycloheptatrienechromium(0) showing rotation about the pseudo three-fold axis.

Fig. 5. ^{13}C NMR spectrum (carbonyl region only) of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ at various temperatures.

pear to be rotating about a pseudo three-fold triene—metal axis (see Fig. 4) at a rate faster than the ^{13}C NMR time constant [39,55,71]. The expected four carbon resonances of the olefin ligand are seen but only one resonance is found for the carbonyl groups. However at lower temperatures [—59°(Cr derivative), —51°(Mo derivative)] this rotation is slowed and two carbonyl resonances in a 1/2 ratio are observed [45]. It is proposed that in the static conformation the unique carbonyl is *trans* to the 3,4-double bond of the olefin.

Aminocarbene · M(CO)$_5$ (M = Cr or W) complexes add HCl or HBr to form derivatives whose structure is still uncertain [74]. Conductivity measurements favor the salt-like structure (b).



$$(CO)_5M{-}C\begin{matrix}\diagup N\begin{matrix}R\\R'\end{matrix}\\ \diagdown R''\end{matrix} + HX \longrightarrow (CO)_5M{-}\underset{\displaystyle XCHR''}{\underset{|}{N}}\begin{matrix}R\\R'\end{matrix} \qquad \text{(a)}$$

$$\text{or} \quad [(CO)_5M{-}X^-]\,[{}^{R}_{R}{>}N{=}CHR''^+] \qquad \text{(b)}$$

The carbonyl shielding data of $(C_6H_{11}NH_2)W(CO)_5$ which would be like structure (a) and the shielding data of $(n\text{-}C_4H_9)_4N[W(CO)_5I]$ which would be like structure (b) are very similar (see Section V). Thus it does not seem possible with the available data to differentiate between the proposed structures on the basis of carbonyl shieldings.

B. Iron, ruthenium and osmium carbonyl derivatives

Again in this group of metals one observes an increase in carbonyl carbon shielding as the atomic weight of the metal increases. The reported terminal carbonyl shieldings for the iron, ruthenium and osmium derivatives have the ranges 221-202, 199-188 and 182-177 ppm respectively.

Compounds of the type $(\pi\text{-}C_5H_5)Fe(CO)_2X$ are the largest class of iron derivatives to be studied thus far. For molecules with an iron—carbon Fe—X bond, the carbonyl shielding is found to obey a linear relationship with Taft σ_I values. For strongly electron-withdrawing X groups the carbonyl carbon resonances are found at higher field. Thus as the available electron density on the metal decreases there is less metal carbonyl back bonding. This trend is consistent with the correlations observed in Group VI metal carbonyls. For molecules where the X group, for an example, is GeR_3 or $PB_{10}H_{12}$, which have Fe—Ge or Fe—P bonds, there is the added possibility of d_π—d_π back donation to these groups from the metal. The observed carbonyl shieldings for these $(\pi\text{-}C_5H_5)Fe(CO)_2X$ derivatives are at higher field that one would expect based solely on electronegativity arguments.

It has been well known for some time through ^1H NMR, infrared and X-ray studies that $(\pi\text{-}C_5H_5)_2Fe_2(CO)_4$ can exist in *cis* and *trans* bridged conformations which are interconverting at room temperature and are static at low temperatures. Recently the dynamic properties of this molecule were revealed in more detail by a variable temeprature ^{13}C NMR study [16]. A schematic line drawing of the ^{13}C NMR results in the carbonyl region are illustrated in Fig. 5. At —85°C there are two carbonyl resonances at 274.7 (bridge) and 210.5 ppm (terminal). When comparing the chemical shifts for the carbonyl derivatives of one transition metal, bridging carbonyl resonances are generally found at lower field than terminal carbonyl resonances. At —73° a third resonance appears at 242 ppm which is centered between the other two peaks. This unusual pattern is explained by the preferential bridge-terminal carbonyl exchange of one of the isomers (the authors prefer the *trans* isomer). At —59° the second isomer begins to participate in bridge-terminal interchange and at some temperature, which is unclear from the

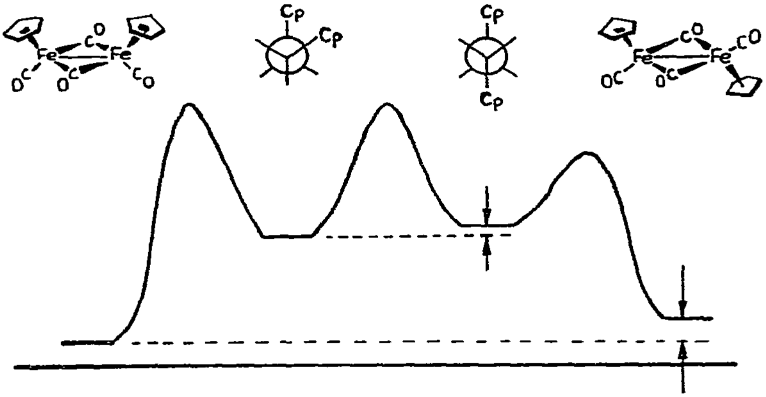


Fig. 6. Schematic diagram of the proposed reaction coordinate for interconversion of *cis*- and *trans*-$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$

available ^{13}C NMR data, *cis—trans* interconversion occurs. In Fig. 6 is shown a proposed reaction coordinate scheme to explain the ^{13}C NMR results. The proposed mechanism involves opening up of a bridged isomer to an all terminal-carbonyl intermediate and then *cis—trans* interconversion via rotation about the iron—iron bond.

It has been observed that *cis—trans* interconversion of $(\pi\text{-}C_5H_5)_2Mo_2(CO)_6$, presumably by rotation about the Mo—Mo metal bond, is a relatively high energy process [51]. This would suggest that such a barrier exists for $(\pi\text{-}C_5H_5)_2Fe_2(CO)$ The iron derivative will have a shorter M—M distance but less interligand steric interactions than the molybdenum compound. Which variable is most important is not known at present. It has been suggested on the basis of a ^{13}C NMR study that bridge-terminal exchange occurs simultaneously with metal—metal bond rotation for $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3P(OC_2H_5)_3$ [81]. In addition it is suggested [81] that at low temperature $[(\pi\text{-}C_5H_5)Ru(CO)_2]_2$ exists as *cis* and *trans* nonbridged isomers. Further clarification of these processes via ^{13}C NMR studies are possible and should be forthcoming soon.

The ^{13}C NMR spectra of several (polyolefin)hexacarbonyldiiron derivatives have been studied at various temperatures [79]. The room temperature ^{13}C NMR spectra of (cycloheptatriene)hexacarbonyldiiron and (bicyclo[6.1.0]-2,4,6-nonatriene)hexacarbonyldiiron each contain two carbonyl resonances with 2/1 relative intensities. These data together with a symmetric pattern for the ^{13}C olefin carbon resonances and invariant ^{1}H NMR spectra at various temperatures suggests that these molecules are not fluxional at room temperature. The structure of (cycloheptatriene)hexacarbonyldiiron has been determined by a single crystal X-ray study [80] and is illustrated in Fig. 7a. If this were the static structure for $(C_7H_8)Fe_2(CO)_6$ in solution three carbonyl resonances of equal area would be expected. The author proposes that two of these resonances are accidentally overlapped to give the two resonances with 2/1 relative intensities. The ^{13}C NMR spectra of the related three molecules shown in Fig. 7b-d each contain only one carbonyl carbon resonance at 30°C [79]. However at —130° the ^{13}C NMR spectrum of the compound in Fig. 7d displays six carbonyl re-

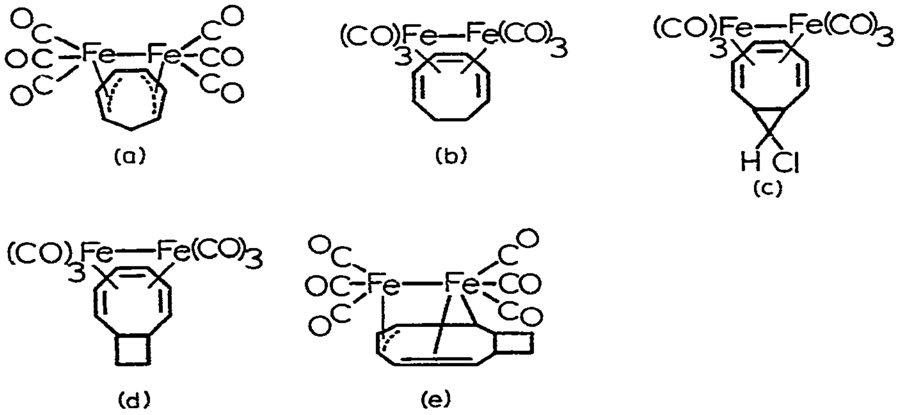


Fig. 7. (a) the solid state structure of $(C_7H_8)Fe_2(CO)_6$; (b)-(d) schematic representation of other (triene)-$Fe_2(CO)_6$ derivatives; (e) proposed low temperature static structure of (bicyclo[6.2.0]-2,4,6-decatriene)Fe_2(C

sonances. This suggests that at 30° the molecule is fluxional and at —130° C the complex has an unsymmetrical static structure possibly like that shown in Fig. 7e.

Attempts to obtain static structure ^{13}C NMR spectra of $Fe(CO)_5$ (—170°) [14] and $(CO)_3Fe(Me_2PCH_2CH_2PMe_2)$ (—80°) [48] were not successful. The first successful example of this type is the ^{13}C NMR spectrum of tricarbonyl (cyclooctatetraene)iron taken at —120° which shows it to be in a static conformation [47]. The spectrum contains two signals in the carbonyl carbon region at 212.4 and 210.3 ppm with intensity ratio 2/1 respectively. The olefin ligand is also static at the low temperature and displays four olefin carbon resonances. It is suggested by the authors that the carbonyl interchange process is independent of the ring atom interchange process at higher temperatures.

Recent reports of the ^{13}C NMR spectra of derivatives of $Ru_3(CO)_{12}$ show the power which this technique will have for structure elucidation of this interesting class of static molecules. As indicated previously, $Ru_3(CO)_{12}$ exhibits two carbonyl resonances of equal intensity at 198.8 and 188.7 ppm. The molecule $H_3Ru_3(CO)_9CMe$, for which the structure in Fig. 8 is proposed, exhibits two carbonyl resonances at 190.1 (area 1) and 189.3 (area 2) ppm [54]. If this structure proves correct, the ^{13}C NMR data allows assignment of equatorial carbonyls to the 188 ppm region in this type of molecule.

C. Rhodium carbonyl derivatives

To date there has been only a limited number of cobalt carbonyl compounds studied. This is due in large part to the sizable quadrupole moment of the cobalt nucleus [^{59}Co(100%), $I = 7/2$] which causes the carbonyl ^{13}C signals to be quite broad. For example, ^{13}C NMR studies of $YCCo_3(CO)_9$ [Y = halogen or alkyl] give only one broad carbonyl resonance. Based on the structure of these compounds, one would expect two carbonyl resonances in a 2/1 ratio which probably would be the case if the resolution were better. Quadrupole broadening is not a problem with rhodium carbonyls [^{103}Rh(100%), $I = \frac{1}{2}$]. In addition to variation of shielding with structure, $^1J(^{103}Rh—^{13}C)$ coupling constants can be used to acquire additional structural information. This can be illustrated by the following two examples. In the ^{13}C NMR spectrum of the novel "diphenyl carbene" complex $[Rh(CPh_2)Cl(C_5H_5N)]_2CO$ both the CO and carbene carbon resonances appear as sharp

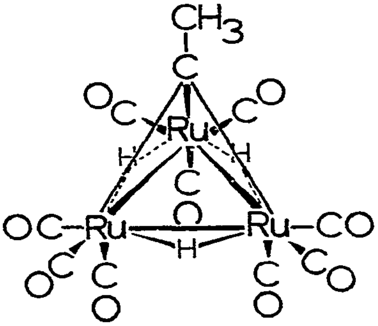
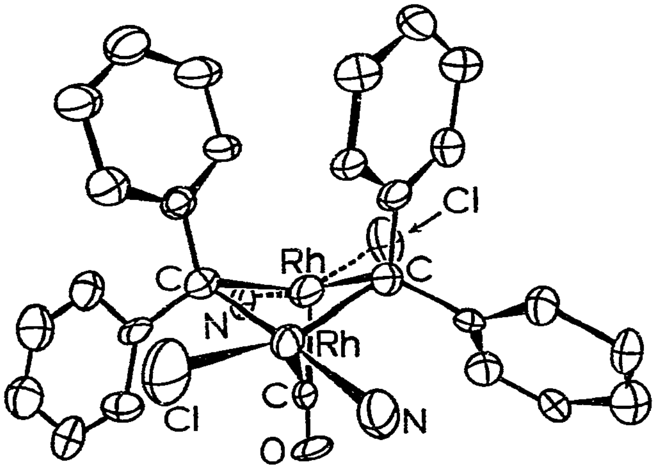


Fig. 8. Proposed structure of $CH_3CRu_3(CO)_9H_3$.



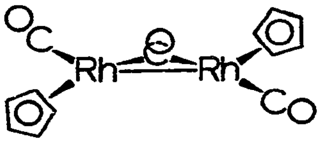


Fig. 9 The solid state structure of $[Rh(CPh_2)Cl(C_5H_5N)]_2CO$. Only the nitrogen atoms of the pyridine rings are included for clarity.

Fig. 10 The solid state structure of $(\pi\text{-}C_5H_5)_2Rh_2(CO)_3$.

triplet signals at room temperature and at —85° C [28]. The carbonyl resonance is at 206.5 ppm which is in the region where bridging carbonyl groups are found. These data suggest that the molecule is static during the NMR measurements and that the carbonyl and carbene ligands are bridging both rhodium atoms. A subsequent X-ray diffraction study confirmed this NMR finding. The structure of this complex is illustrated in Fig. 9.

The ^{13}C NMR of the carbonyl region of *trans*-$(Ph_3P)_2Rh(CO)Cl$ at —14° exhibits a doublet with triplet structure [89]. The doublet is due to ^{103}Rh—^{13}C coupling and the triplet to ^{31}P—^{13}C coupling. As the temperature is increased the doublet loses the triplet fine structure which suggests rapid phosphine exchange. At + 94° the carbonyl resonance becomes a singlet suggesting carbonyl exchange.

Recent ^{13}C NMR studies of polynuclear rhodium carbonyl compounds has partially clarified the interesting dynamic properties of these molecules in solution. One of the first compounds studied in this area was $(\pi\text{-}C_5H_5)_2Rh_2(CO)_3$ which has the solid state structure shown in Fig. 10. At 20° C the carbonyl region of the ^{13}C NMR spectrum of this compound contains only a sharp triplet at 203.8 ppm ($J(^{103}Rh$—$^{13}C)$ 43 Hz) [37]. This suggests that the molecule is unde going rapid intramolecular exchange of the two types of carbonyl groups. At —80° the carbonyl region of the ^{13}C NMR spectrum changes to a sharp triplet at 231.8 ppm ($J(^{103}Rh$—$^{13}C)$ 45 Hz) (area 1) and a doublet at 191.8 ppm ($J(^{103}Rh$—$^{13}C)$ 83 Hz) (area 2). The low temperature result correlates well with the solid state structure and strongly suggests that the low field resonance is due to the bridging carbonyl group. As expected the weighted average of the low temperature chemical shifts is in agreement with the chemical shift value at 20°. Also there is consistency in the weighted average of the low temperature coupling constants (see Section V).

A NMR study of a trinuclear rhodium complex which apparently contains

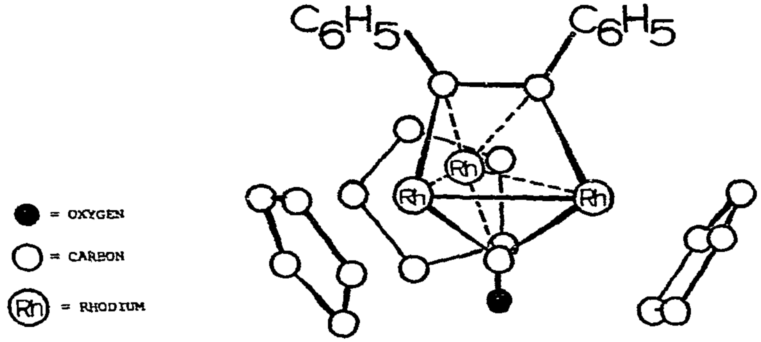


Fig. 11. The solid state structure of $(\pi\text{-}C_5H_5)_3Rh_3(PhC{\equiv}CPh)CO$.

a carbonyl group bridging all three metal atoms has been reported [49]. The room temperature ^{13}C NMR spectrum of $(\pi\text{-}C_5H_5)_3Rh_3(PhC{\equiv}CPh)CO$ which is ^{13}C-enriched in the carbonyl group exhibits a quartet signal at 236 ppm ($J(^{103}Rh—^{13}C)$ 38.7 Hz) for the carbonyl carbon. At −88° the carbonyl signal changes to a triplet with doublet character. These ^{13}C NMR data suggest that the carbonyl group is in a static unsymmetrical triple-bridging position. The carbonyl carbon is more strongly coupled to two of the rhodium nuclei [triplet; ($J(^{103}Rh—^{13}C)$ 43.7 Hz)] and less strongly coupled to the third rhodium nucleus [doublet; ($J(^{103}Rh—^{13}C)$ 28.4 Hz)]. These low temperature results are consistent with the unsymmetrical triple-bridging configuration of the carbonyl group (see Fig. 11) found in the X-ray structure study.

V. ^{13}C NMR chemical shift data for the transition metal carbonyl compounds

Compound	Solvent^a	$\delta(CO)^b$		References and remarks
		$\delta(CO)_{trans}$	$\delta(CO)_{cis}$	
Vandium compounds				
$[V(CO)_6][Na(diglyme)_2]$	THF	225.7		15,19 ($J(^{51}V—^{13}C)$ 116Hz)
Chromium compounds				
$Cr(CO)_6$	CH_2Cl_2	212.5		17
	CH_2Cl_2	211.7		55
	$CHCl_3$	211.2		15
	$CDCl_3/C_6F_6$	212.1		20, 22
	CCl_4	210.7		55
	C_6F_6	214.6		20
	THF	212.5		15
	CH_3CN	212.5		55
	$CHCl_3$	212.3		71
$(CH_3CN)Cr(CO)_5$	CH_2Cl_2	219.2	213.9	55
$Ph_3PCr(CO)_5$	$CHCl_3$	221.3	216.5	15
$(PhO)_3PCr(CO)_5$	$CHCl_3$	217.5	213.8	15
trans-$[(MeO)_3P]_2Cr(CO)_4$	CH_2Cl_2	219.3		55 ($J(^{31}P—^{13}C)$ 19.6 Hz)

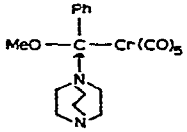
(continued)

^{13}NMR Chemical Shift Data *(continued)*

Compound	Solvent[a]	δ(CO)[b]		References and remarks
		$\delta(CO)_{trans}$	$\delta(CO)_{cis}$	
trans-$[(PhO)_3P]_2Cr(CO)_4$	$CHCl_3$	216.6		15
$(CO)_5CrC(NH_2)Me$	$CHCl_3$	223.1	217.4	23
$(CO)_5CrC(OMe)Me$	CH_2Cl_2	223.8	216.7	55
	$CHCl_3$	223.6[d]	217.4[d]	24, 22, 23, 30
	THF	224.3[d]	217.3[d]	55, 24
	C_6H_6	223.5[d]	216.7[d]	55, 25
$(CO)_5CrC(MeNH)Me$	THF	223	218	24
	$CDCl_3/C_6F_6$	224.4	219.2	22
$(CO)_5CrC(OMe)C_2H_3$	$CHCl_3$	224.0	216.4	31
$(CO)_5CrC(OEt)Me$	THF	226	217	24
	$CHCl_3$	223.4	216.3	23
	$CHCl_3$	224	218	24
$(CO)_5CrC(NMe_2)Me$	THF	224	218	24
	$(CH_3)_2CO$	224.4	218.9	74
$(CO)_5CrC(NH_2)Th$[b]	$CDCl_3/C_6F_6$	226.2	220.8	22
$(CO)_5CrC(NH_2)Fu$[c]	$CDCl_3/C_6F_6$	224.7	219.5	22
$(CO)_5CrC(i\text{-}PrNMe)Me$	THF	224.0	218.0	24
$(CO)_5CrC(NH_2)\text{-}p\text{-}BrC_6H_4$	THF	224.0	218.1	23
	$CHCl_3$	223.2	216.9	23
cis-$(CO)_4Cr[C(SMe)_2]_2$	C_6F_6	227.0	215.9	68, 40
$(CO)_5CrC(NH_2)Ph$	$CHCl_3$	223.4	217.3	23
	THF	224.4	218.5	23
$(CO)_5CrC(OEt)Th$[b]	$CDCl_3/C_6F_6$	224.9	218.7	22
$(CO)_5CrC(OEt)Fu$[c]	$CDCl_3/C_6F_6$	225.5	218.4	22
$(CO)_5CrC(OMe)\text{-}p\text{-}BrC_6H_4$	$CHCl_3$	223.7	215.9	23
$(CO)_5CrC(OMe)\text{-}p\text{-}ClC_6H_4$	$CDCl_3/C_6F_6$	224.9	217.3	22
	$CHCl_3$	223.7	215.9	23
$(CO)_5CrC(OMe)m\text{-}ClC_6H_4$	$CHCl_3$	223.6	215.7	23
$(CO)_5CrC(OMe)\text{-}p\text{-}FC_6H_4$	$CHCl_3$	223.6	216.1	23
$(CO)_5CrC(OMe)Ph$	C_6H_6	224.6	216.7	25, 26
	$CDCl_3/C_6F_6$	226.0	218.4	22
	C_6H_6	225.0	217.0	24
	$CHCl_3$	224.1	216.1	23
$(CO)_5CrC(NH_2)\text{-}p\text{-}MeC_6H_4$	THF	224.4	218.6	23
	$CHCl_3$	223.7	217.5	23
$(CO)_5CrC(MeNH)Ph$	THF	224.0	218.0	24
	$(CH_3)_2CO$	224.6	218.4	74
$(CO)_5CrC[N(CH_2)_4]CH_3$	C_6H_6	223.8	218.7	74
$(CO)_5CrC[N(CH_2)_4]Ph$	$(CH_3)_2CO$	224.7	218.5	74
$(CO)_5CrC(OMe)\text{-}p\text{-}CF_3C_6H_4$	$CHCl_3$	223.7	215.5	23
$(CO)_5CrC(OMe)\text{-}m\text{-}CF_3C_6H_4$	$CHCl_3$	223.6	215.6	23
$(CO)_5CrC(OMe)\text{-}p\text{-}MeC_6H_4$	$CHCl_3$	223.8	216.3	23
$(CO)_5CrC(OEt)Ph$	$CHCl_3$	224.2	216.1	23
	THF	226.0	218.0	24
$(CO)_5CrC(OMe)\text{-}p\text{-}OMeC_6H_4$	$CHCl_3$	223.7	216.8	23
	$CDCl_3/C_6F_6$	225.5	218.4	22
$(CO)_5CrC(OMe)\text{-}m\text{-}OMeC_6H_4$	$CHCl_3$	223.9	215.8	23
$(CO)_5CrC(NMe_2)Ph$	$CDCl_3/C_6F_6$	225.2	218.7	22
	$(CH_3)_2CO$	224.6	218.2	74
$(CO)_5CrC(NC_4H_8)Th$[b]	$CDCl_3/C_6F_6$	224.9	218.7	22
$(CO)_5CrC(NC_4H_8)Fu$[c]	$CDCl_3/C_6F_6$	225.5	219.2	22
$(CO)_5CrC(NHC_6H_{11})Et$	$CDCl_3/C_6F_6$	224.4	219.8	22
$(CO)_5CrC(NC_4H_8)Ph$	$CDCl_3/C_6F_6$	225.5	219.2	22
$(CO)_5CrC(NC_5H_{10})Ph$	$CDCl_3/C_6F_6$	225.5	218.4	22
$(CO)_5CrC(OEt)ferrocenyl$	$CDCl_3/C_6F_6$	224.1	218.7	22

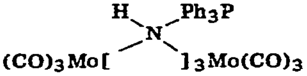
(continued)

^{13}NMR Chemical Shift Data *(continued)*

<table>
<tr><th rowspan="2">Compound</th><th rowspan="2">Solvent^a</th><th colspan="2">$\delta(CO)^b$</th><th rowspan="2">References and remarks</th></tr>
<tr><th>$\delta(CO)_{trans}$</th><th>$\delta(CO)_{cis}$</th></tr>
<tr><td>$[(CO)_5CrC(O)Th]\,NMe_4{}^b$</td><td>$(CH_3)_2CO$</td><td>227.6</td><td>223.6</td><td>22</td></tr>
<tr><td>$(\pi\text{-}C_6H_6)Cr(CO)_3$</td><td>$CH_2Cl_2$</td><td colspan="2">223.8</td><td>30</td></tr>
<tr><td></td><td>CH_2Cl_2</td><td colspan="2">233.3</td><td>40</td></tr>
<tr><td>$(\pi\text{-}ClC_6H_5)Cr(CO)_3$</td><td>$CH_2Cl_2$</td><td colspan="2">231.9</td><td>40</td></tr>
<tr><td>$(\pi\text{-}FC_6H_5)Cr(CO)_3$</td><td>$CH_2Cl_2$</td><td colspan="2">232.0</td><td>40</td></tr>
<tr><td>$(\pi\text{-}NH_2C_6H_5)Cr(CO)_3$</td><td>$CH_2Cl_2$</td><td colspan="2">234.6</td><td>40</td></tr>
<tr><td>$(\pi\text{-}MeC_6H_5)Cr(CO)_3$</td><td>$CH_2Cl_2$</td><td colspan="2">233.6</td><td>40</td></tr>
<tr><td>$(\pi\text{-}MeOC_6H_5)Cr(CO)_3$</td><td>$CH_2Cl_2$</td><td colspan="2">233.5</td><td>40</td></tr>
<tr><td>$(\pi\text{-}MeCO_2C_6H_5)Cr(CO)_3$</td><td>$CH_2Cl_2$</td><td colspan="2">231.2</td><td>40</td></tr>
<tr><td>$(\pi\text{-}Me_2NC_6H_5)Cr(CO)_3$</td><td>$CH_2Cl_2$</td><td colspan="2">235.0</td><td>40</td></tr>
<tr><td>$(\pi\text{-n-}BuOC_6H_5)Cr(CO)_3$</td><td>$CH_2Cl_2$</td><td colspan="2">233.6</td><td>40</td></tr>
<tr><td>$(\pi\text{-mesitylene})Cr(CO)_3$</td><td>$CH_2Cl_2$</td><td colspan="2">235.1</td><td>39, 71</td></tr>
<tr><td>$(\pi\text{-durene})Cr(CO)_3$</td><td>$CH_2Cl_2$</td><td colspan="2">235.5</td><td>39</td></tr>
<tr><td></td><td></td><td colspan="2">235.5</td><td>71</td></tr>
<tr><td>$(\pi\text{-hexamethylbenzene})Cr(CO)_3$</td><td>$CH_2Cl_2$</td><td colspan="2">236.3</td><td>71</td></tr>
<tr><td>$(\pi\text{-}trans\text{-1,3-dimethylindane})\text{-}Cr(CO)_3$</td><td>$CDCl_3/C_6F_6$</td><td colspan="2">235.0</td><td>52</td></tr>
<tr><td>$(\pi\text{-cycloheptatriene})Cr(CO)_3$</td><td>$CH_2Cl_2$</td><td colspan="2">232.7</td><td>39</td></tr>
<tr><td></td><td>$(CH_3)_2CO$</td><td colspan="2">232.6</td><td>45, −1°C</td></tr>
<tr><td></td><td>$(CH_3)_2CO$</td><td>241.3
(area 1)</td><td>230.1
(area 2)</td><td>−59°C</td></tr>
<tr><td></td><td>CH_2Cl_2</td><td colspan="2">232.7</td><td>71</td></tr>
<tr><td>$(CO)_5CrCNCH(Me_2)$</td><td>$CDCl_3/C_6F_6$</td><td>218.2</td><td>216.3</td><td>22</td></tr>
<tr><td>$(CO)_5CrCN(p\text{-}MeC_6H_4)$</td><td>$CDCl_3/C_6F_6$</td><td>218.7</td><td>216.5</td><td>22</td></tr>
<tr><td> </td><td>$(CH_3)_2CO$</td><td>228.5</td><td>223.8</td><td>26</td></tr>
<tr><td>$\{[1,7\text{-}B_9H_8CHPCr(CO)_5]_2Fe\}\text{-}(Me_4N)_2$</td><td>$CH_3CN$</td><td>223.9</td><td>217.5</td><td>59 $cis(J(^{31}P—^{13}C)$ 12 Hz</td></tr>
<tr><td>$(\text{norbornadiene})Cr(CO)_4$</td><td>$CH_2Cl_2$</td><td>234.5</td><td>226.8</td><td>71</td></tr>
<tr><td>$[(CO)_5CrBr]\,[Me_2{=}CHMe]$</td><td>$(CH_3)_2CO$</td><td>225.1</td><td>216.9</td><td>74</td></tr>
<tr><td>$[(CO)_5CrBr]\,[$  $N{=}CHMe]$</td><td>$(CH_3)_2CO$</td><td>225.2</td><td>217.0</td><td>74</td></tr>
<tr><td>$[(CO)_5CrBr]\,[MeNH{=}CHPh]$</td><td>$(CH_3)_2CO$</td><td>225.5</td><td>217.3</td><td>74</td></tr>
<tr><td>$[(CO)_5CrBr]\,[Me_2N{=}CHPh]$</td><td>$(CH_3)_2CO$</td><td>225.6</td><td>217.6</td><td>74</td></tr>
<tr><td>$[(CO)_5CrBr]\,[$  $N{=}CHPh]$</td><td>$(CH_3)_2CO$</td><td>225.7</td><td>217.7</td><td>74</td></tr>
<tr><td>$[(CO)_5CrCl]\,[$  $N{=}CHMe]$</td><td>$(CH_3)_2CO$</td><td>223.8</td><td>217.6</td><td>74</td></tr>
<tr><td>$Na[\pi\text{-}C_5H_5Cr(CO)_3]$</td><td>THF</td><td>246.7</td><td></td><td>15</td></tr>
<tr><td>Molybdenum compounds</td><td></td><td></td><td></td><td></td></tr>
<tr><td>$Mo(CO)_6$</td><td>CH_2Cl_2</td><td colspan="2">202.0</td><td>17</td></tr>
<tr><td></td><td>$CHCl_3$</td><td colspan="2">200.7</td><td>15</td></tr>
<tr><td></td><td>$CDCl_3/C_6F_6$</td><td colspan="2">202.0</td><td>20</td></tr>
<tr><td></td><td>C_6F_6</td><td colspan="2">204.1</td><td>20</td></tr>
<tr><td></td><td>$CHCl_3$</td><td colspan="2">204.1</td><td>71 $(J(^{95}Mo—^{13}C)$ 68 Hz)</td></tr>
<tr><td>$(MeO)_3PMo(CO)_5$</td><td>neat</td><td>209.2</td><td>206.4</td><td>20 $trans(J(^{31}P—^{13}C)$ 18.3Hz)
$cis(J(^{31}P—^{13}C)$ 7.3 Hz)</td></tr>
<tr><td>$(EtO)_3PMo(CO)_5$</td><td>neat</td><td>208.7</td><td>206.8</td><td>20 $trans\ J(^{31}P—^{13}C)$ 18.9 Hz
$cis\ J(^{31}P—^{13}C)$ 6.7 Hz</td></tr>
<tr><td>$(i\text{-}PrO)_3PMo(CO)_5$</td><td>neat</td><td>209.7</td><td>206.3</td><td>20, 30
$trans(J^{31}P—^{13}C)$ 12.2 Hz)
$cis(J^{31}P—^{13}C)$ 14.6 Hz)</td></tr>
</table>

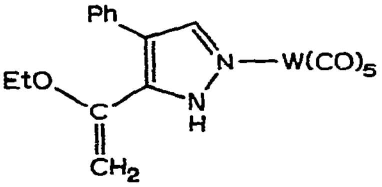
(continued)

^{13}NMR Chemical Shift Data *(continued)*

Compound	Solvent^a	$\delta(CO)^b$		References and remarks
		$\delta(CO)_{trans}$	$\delta(CO)_{cis}$	
$Ph_3PMo(CO)_5$		211.0	206.5	20, 33
trans-$[(MeO)_3P]_2Mo(CO)_4$		210.3		20(J(^{31}P—^{13}C) 13.4 Hz)
(diphos)$Mo(CO)_4$	$CDCl_3/C_6F_6$	218.5	210.6	20 *trans*(J(^{31}P—^{13}C) 24 Hz) *cis*(J(^{31}P—^{13}C) 8.4 Hz)
(π-cycloheptatriene)$Mo(CO)_3$	CH_2Cl_2	220.5^d		39, 55, 71
	$(CH_3)_2CO$	220.7		45, 27°C
	$(CH_3)_2CO$	229.2	217.9	−51°C
		(area 1)	(area 2)	
[(π-cycloheptatrienyl)$Mo(CO)_3$]PF_6	CH_3CN	206.7		55
(π-*m*-xylene)$Mo(CO)_3$	$CHCl_3$	223.1		30
(π-mesitylene)$Mo(CO)_3$	CH_2Cl_2	223.7		39, 71
(π-durene)$Mo(CO)_3$	CH_2Cl_2	224.4		39, 71
(π-hexamethylbenzene)$Mo(CO)_3$	CH_2Cl_2	225.9		71
(π-norbornadiene)$Mo(CO)_4$	$CHCl_3$	214.8	218.4	19
	CH_2Cl_2	214.4	217.8	19
	CH_2Cl_2	215.0	218.0	71
[(π-C_5H_5)$Mo(CO)_3$]$_2$	CH_2Cl_2	233.9	227.1	55 (broad resonances)
	CH_2Cl_2	233.7	225.2	−85°C
		(area 1)	(area 2)	55,
	p-xylene	228.6		100°C
(π-C_5H_5)$Mo(CO)_2NO$	CH_2Cl_2	226.9^d		19, 55, 15
(π-C_5H_5)$Mo(CO)_3Cl$	CH_2Cl_2	225.0		19
[7, 9-$B_9H_{10}CHPMo(CO)_5$]Me_4N	CH_3CN	209.7	205.1	58, 59 *trans*(J^{31}(P—^{13}C) 26 H *cis*(J(^{31}P—^{13}C) 8 Hz)
		218.4		55
(n-$C_4H_9)_4N[Mo(CO)_5I]$	$CHCl_2$	214.4	202.4	55
Tungsten complexes				
$W(CO)_6$	CH_2Cl_2	192.1		17(J(^{183}W—^{13}C) 126Hz)
	$CHCl_3$	191.4		15
	$CDCl_3/C_6F_6$	192.1		20, 22 (J(^{183}W—^{13}C) 125Hz)
	C_6F_6	193.7		20 (J(^{183}W—^{13}C) 125Hz)
	$CHCl_3$	191.9		71 (J(^{183}W—^{13}C) 126Hz)
$(MeO)_3PW(CO)_5$	neat	199.5	196.5	20 *trans*(J(^{183}W—^{13}C) 139.1H *cis*(J(^{183}W—^{13}C) 125.1 Hz *trans*(J(^{31}P—^{13}C) 37.2 Hz) *cis*(J(^{31}P—^{13}C) 11.6 Hz)
	neat	198.8	196.2	71 *trans*(J(^{183}W—^{13}C) 135 Hz *cis*(J(^{183}W—^{13}C) 123 Hz) *trans*(J(^{31}P—^{13}C) 36 Hz) *cis*(J(^{31}P—^{13}C) 10 Hz)
$(C_6H_{11}NH_2)W(CO)_5$	CH_2Cl_2	201.9	199.1	17, 20 *cis*(J(^{183}W—^{13}C) 132 Hz)
$Et_3PW(CO)_5$		200.2	198.5	20 *trans*(J(^{183}W—^{13}C) 140 Hz *cis*(J(^{183}W—^{13}C) 127 Hz) *trans*(J(^{31}P—^{13}C) 19 Hz) *cis*(J(^{31}P—^{13}C) 6 Hz)

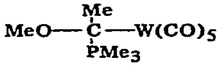
(continued)

^{13}NMR Chemical Shift Data *(continued)*

Compound	**Solvent**[a]	**δ(CO)**[b]		**References and remarks**
		δ(CO)$_{trans}$	δ(CO)$_{cis}$	
	neat	200.2	198.5	71 *trans*(J(^{183}W—^{13}C) 142 Hz) *cis*(J(^{183}W—^{13}C) 129 Hz) *trans*(J(^{31}P—^{13}C) 19 Hz) *cis*(J(^{31}P—^{13}C) 6 Hz)
$(EtO)_3PW(CO)_5$	neat	199.6	197.2	20 *trans*(^{183}W—^{13}C) 138.5 Hz) *cis*(J(^{183}W—^{13}C) 125.1 Hz) *trans*(J(^{31}P—^{13}C) 36.6 Hz) *cis*(J(^{31}P—^{13}C) 10.9 Hz)
$(n\text{-}Bu)_3PW(CO)_5$	neat	200.4	198.6	20 *trans*(J(^{183}W—^{13}C) 142.1 Hz) *cis*(J(^{183}W—^{13}C) 124.4 Hz) *trans*(J(^{31}P—^{13}C) 18.9 Hz) *cis*(J(^{31}P—^{13}C) 7.3 Hz)
	$CDCl_3/C_6F_6$	200.4	198.6	22 *trans*(J(^{183}W—^{13}C) 140 Hz) *cis*(J(^{183}W—^{13}C) 122 Hz)
$(n\text{-}BuO)_3PW(CO)_5$	CH_2Cl_2	198.8	196.1	17, 20 *trans*(J(^{31}P—^{13}C) 36 Hz) *cis*(J(^{31}P—^{13}C) 9 Hz)
$[(n\text{-}BuO)_2Ph]PW(CO)_5$	CH_2Cl_2	200.0	196.9	17 *trans* (J(^{31}P—^{13}C) 29 Hz) *cis*(J(^{31}P—^{13}C) 9 Hz)
$[(n\text{-}BuO)Ph_2]PW(CO)_5$	$CHCl_2$	199.0	197.5	17 *trans*(J^{31}P—^{13}C) 27 Hz) *cis*(J(^{31}P—^{13}C) 9 Hz)
$Ph_3PW(CO)_5$	CH_2Cl_2	199.8	198.0	17, 20 *cis*(J(^{183}W—^{13}C) 129 Hz) *trans*(J(^{31}P—^{13}C) 22 Hz) *cis*(J(^{31}P—^{13}C) 7 Hz)
$(PhO)_3PW(CO)_5$	CH_2Cl_2	197.0	194.5	17, 20 *trans*(J(^{31}P—^{13}C) 45.4 Hz) *cis*(J(^{31}P—^{13}C) 10.5 Hz)
$Ph_3AsW(CO)_5$	CH_2Cl_2	199.7	197.5	17, 20 *cis*(J(^{183}W—^{13}C) 124 Hz)
$Ph_3BiW(CO)_5$	CH_2Cl_2	198.3	197.8	17 *cis*(J(^{183}W—^{13}C) 126 Hz)
$Ph_3SbW(CO)_5$	CH_2Cl_2	199.1	197.0	17 *cis*(J(^{183}W—^{13}C) 127 Hz)
$(diphos)W(CO)_4$		not observed	204.6	20 *cis*(J(^{31}P—^{13}C) 9 Hz)
		202.4	198.6	46
cis-$(PEt_3)_2W(CO)_4$	CH_2Cl_2	204.7	204.4	71 *trans*(J(^{31}P—^{13}C) 15.2 Hz) *cis*(J(^{31}P—^{13}C) 6.3 Hz)
trans-$(PEt_3)_2W(CO)_4$	CH_2Cl_2	204.7		71 (J(^{31}P—^{13}C) 5 Hz)
fac-$[Et_3P]_3W(CO)_3$	CH_2Cl_2	212.4		20 (J(^{183}W—^{13}C) 135 Hz) 71 *trans*(J(^{31}P—^{13}C) 14 Hz) *cis*(J(^{31}P—^{13}C) 5 Hz)
$(CO)_5WC(MeNH)Me$	C_6H_6	203.4	198.9	25 *cis* isomer
	C_6H_6	203.4	199.4	25 *trans* isomer
$(CO)_5WC(OEt)Me$	$CHCl_3$	203.4	197.2	23
$(CO)_5WC(OH)Me$	CH_2Cl_2	not observed	197.2	29
$(CO)_5WC(NH_2)Me$	$CHCl_3$	203.8	198.5	23
$(CO)_5WC(SMe)Me$	C_6H_6	207.4	198.1	25

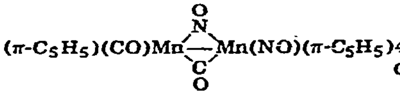
(continued)

^{13}NMR Chemical Shift Data *(continued)*

Compound	Solvent^a	δ(CO)^b		References and remarks
		δCO)$_{trans}$	δ(CO)$_{cis}$	
$(CO)_5WC(OMe)Me$	C_6H_6	203.6	197.6	27, 25 *cis*(J(^{183}W—^{13}C) 127 Hz)
	$CHCl_3$	203.4	197.2	23
$(CO)_5WC(OH)Ph$	CH_2Cl_2	203.5	197.4	29
$(CO)_5WC(NH_2)Ph$	$CHCl_3$	203.8	198.2	23
$(CO)_5WC(OMe)$-*p*-BrC_6H_4	CH_2Cl_2	203.7	197.3	23
$(CO)_5WC(OMe)$-*p*-ClC_6H_4	CH_2Cl_2	203.7	197.3	23
$(CO)_5WC(OMe)$-*p*-FC_6H_4	CH_2Cl_2	203.5	197.4	23
$(CO)_5WC(OMe)Ph$	$CHCl_3$	203.6	197.2	23
	$CDCl_3/C_6F_6$	204.6	198.6	20, 22
	CH_2Cl_2	204.2	197.8	23
$(CO)_5WC(OMe)$-*p*-$CF_3C_6H_4$	CH_2Cl_2	203.9	197.1	23
$(CO)_5WC(OEt)Ph$	$CHCl_3$	203.5	197.2	23
$(CO)_5WC(OMe)$-*p*-MeC_6H_4	CH_2Cl_2	203.8	197.8	23
$(CO)_5WC(OMe)$-*p*-$MeOC_6H_4$	CH_2Cl_2	203.4	197.9	23
$(CO)_5WC[N(CH_3)_2]CH_3$	$(CH_3)_2CO$	204.3	199.7	74
$(CO)_5WC[N(CH_3)(C_2H_5)]CH_3$	$(CH_3)_2CO$	204.22	199.7	74
(two isomers)		204.22	199.9	
$(CO)_5WC(SeCH_3)CH_3$	$(CH_3)_2CO$	205.0	197.8	75
(π-cycloheptatriene)$W(CO)_3$	CH_2Cl_2	211.6		39, 71
(π-cyclooctatetraene)$W(CO)_3$	C_6F_5Br	193.8		52
(π-mesitylene)$W(CO)_3$	CH_2Cl_2	212.6		39, 71
(π-hexamethylbenzene)$W(CO)_3$	CH_2Cl_2	215.7		71
(π-durene)$W(CO)_3$	CH_2Cl_2	213.7		39(J(^{183}W—^{13}C) 189 Hz)
	CH_2Cl_2	213.7		71
(π-norbornadiene)$W(CO)_4$	$CHCl_3$	209.4	203.6	15
$Br(CO)_4W{\equiv}C{-}CH_3$	CH_2Cl_2	192.7		32
$Cl(CO)_4W{\equiv}C{-}CH_3$	CH_2Cl_2	194.0		32
$I(CO)_4W{\equiv}C{-}CH_3$	CH_2Cl_2	191.7		32
(π-C_5H_5)$W(CO)_3Me$	$CHCl_3$	217.8	239.2	30
 $MeO{-}\overset{Me}{\underset{PMe_3}{C}}{-}W(CO)_5$	$(CH_3)_2CO$	203.6	203.0	27 *cis*(J(^{183}W—^{13}C) 128 Hz)
$[HW_2(CO)_{10}][Ph_3P{=}N{=}PPh_3]$	CH_2Cl_2	201.4	198.9	55
(π-C_5H_5)$W(CO)_2PMe_3SnMe_3$	C_6H_6	223.0		70, 77
(π-C_5H_5)$W(CO)_2PMe_2PhSnMe_3$	C_6H_6	223.2		70, 77
(π-C_5H_5)$W(CO)_2PMePh_2SnMe_3$	C_6H_6	223.3		70, 77
(π-C_5H_5)$W(CO)_2P(OMe)_3SnMe_3$	C_6H_6	220.6		70, 77
(π-C_5H_5)$W(CO)_2P(OPh)_3SnMe_3$	C_6H_6	220.5		70, 77
$[(CO)_5WBr][Me_2N{=}CHMe]$	$(CH_3)_2CO$	201.9	198.9	74^e
$[(CO)_5WBr][{}^{Me}_{Et}{>}N{=}CHMe]$	$(CH_3)_2CO$	202.0	199.0	74^e
$(n\text{-}C_4H_9)_4N[W(CO)_5I]$	CH_2Cl_2	201.9	196.6	55 *cis*(J(^{183}W—^{13}C) 129 Hz)
Manganese compounds				
$Mn_2(CO)_{10}$	$CHCl_3$	223.1	212.9	55 (broad resonances)
$MeMn(CO)_5$	CH_2Cl_2	213.4		36
(π-C_5H_5)$Mn(CO)_3$	CH_2Cl_2	225.7		55
		220.4		19
	$CHCl_3$	224.9		76
		225.1		15
(π-$C_5H_4CH_3$)$Mn(CO)_3$	CH_2Cl_2	225.4		36
	$CHCl_3$	224.4		76
(π-$C_5H_4CO_2CH_3$)$Mn(CO)_3$	$CHCl_3$	222.7		76
(π-$C_5H_4COCH_3$)$Mn(CO)_3$	$CHCl_3$	223.2		76
(π-$C_5H_4CH_2CH_3$)$Mn(CO)_3$	$CHCl_3$	224.7		76

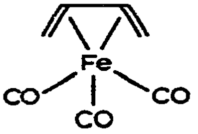
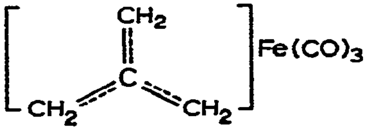
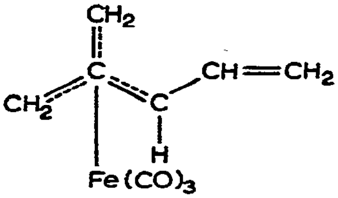
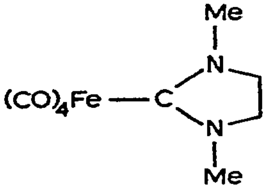
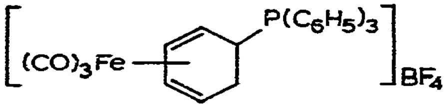
(continued)

^{13}NMR Chemical Shift Data *(continued)*

Compound	Solvent[a]	δ(OC)[b] δ(OC)$_{trans}$	 δ(OC)$_{cis}$	References and remarks
[π-$C_5H_4CH(CH_3)_2$]Mn(CO)$_3$	$CHCl_3$	225.1		76
[π-$C_5H_4C(CH_3)_3$]Mn(CO)$_3$	$CHCl_3$	225.3		76
(π-C_5H_5)Mn(CO)$_2$PPh$_3$	$CHCl_3$	223.3		76
(π-C_5H_5)Mn(CO)$_2$AsPh$_3$	$CHCl_3$	232.4		76
(π-C_5H_5)Mn(CO)$_2$SbPh$_3$	$CHCl_3$	230.8		76
(π-C_5H_5)Mn(CO)$_2$P(OPh)$_3$	$CHCl_3$	226.4		76
(π-C_5H_5)Mn(CO)$_2$P(C_6H_{11})$_3$	$CHCl_3$	230.7		76
(π-C_5H_5)Mn(CO) (diphos)	$CHCl_3$	220.5		76
 (π-C_5H_5)(CO)Mn(μ-NO)(μ-CO)Mn(NO)(π-C_5H_5)	4/1/1 toluene / CH_2Cl_2/C_6F_6	268 217	*trans* isomer	67, —40°
		267 214	*cis* isomer	
Rhenium compounds				
$Re_2(CO)_{10}$	THF	183.7	192.7	55, —60°C
Iron compounds				
$Fe(CO)_5$	neat	209.0		12, 88
	neat	211.9		13(J(^{57}Fe—^{13}C) 23.4 Hz)
	C_6H_6	213.6 ± 3		12, 88
	C_6H_6	210.5		55
	THF	211.0		55
	CH_3CN	211.6		55
$Fe_3(CO)_{12}$	CH_2Cl_2	212.5		16
(pyridine)Fe(CO)$_4$	THF	217.0		55
$Ph_3PFe(CO)_4$	CH_2Cl_2	213.4		55(J(^{31}P—^{13}C) 22 Hz)
$(Ph_3P)_2Fe(CO)_3$	CH_2Cl_2	214.3		55(J(^{31}P—^{13}C) 29.5 Hz)
[(π-C_5H_5)Fe(CO)$_2$]$_2$	CH_2Cl_2	242.6		16 55°C
	CH_2Cl_2	210.5 (area 1)	274.7 (area 2)	—85°C
[(π-C_5H_5)Fe(CO)$_2$][Ph$_3$P=N=PPh$_3$]	CH_2Cl_2	214.4		55
[(π-C_5H_5)Fe(CO)$_3$]PF$_6$	$(CH_3)_2CO$	202.9		15
(π-C_5H_5)Fe(CO)$_2$Br	CH_2Cl_2	213.5		38
	$CHCl_3$	213.2		30
(π-C_5H_5)Fe(CO)$_2$Cl	CH_2Cl_2	213.3		38
	$CHCl_3$	212.9		30
(π-C_5H_5)Fe(CO)$_2$I	CH_2Cl_2	213.6		38
	$CHCl_3$	213.6[d]		30, 19
[(π-C_5H_5)Fe(CN)$_2$(CO)]K	H_2O	219.2		30
(π-C_5H_5)Fe(CO)$_2$(CN)	CH_2Cl_2	211.4		38
	$CHCl_3$	211.1		30
(π-C_5H_5)Fe(CO)$_2$Me	CH_2Cl_2	218.3		38
	$CHCl_3$	218.4		30
(π-C_5H_5)Fe(CO)$_2$COCH$_3$	$CHCl_3$	215.7		30
(π-C_5H_5)Fe(CO)$_2$Et	CH_2Cl_2	218.6		38
(π-C_5H_5)Fe(CO)$_2$CH$_2$CH=CH$_2$	$CH_3C_6H_5$	216.0		61
(π-C_5H_5)Fe(CO)$_2$GeMe$_3$	CH_2Cl_2	213.2		38
(π-C_5H_5)Fe(CO)$_2$SiMe$_3$	CH_2Cl_2	216.5		38
(π-C_5H_5)Fe(CO)$_2$SnMe$_3$	CH_2Cl_2	215.7		38
(π-C_5H_5)Fe(CO)$_2$(σ-C_5H_5)	$CH_3C_6H_5$	216.1		61
(π-C_5H_5)Fe(CO)$_2$C$_6$F$_5$	CH_2Cl_2	214.6		38
(π-C_5H_5)Fe(CO)$_2$-p-ClC$_6$H$_4$	CH_2Cl_2	216.8		38

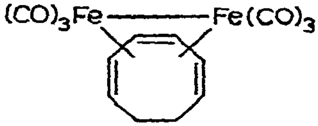
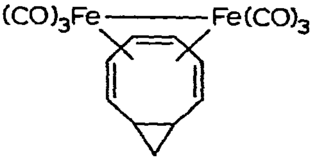
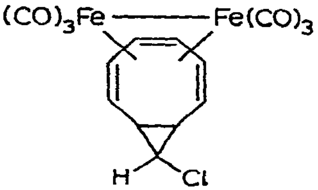
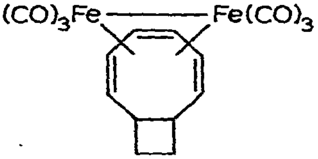
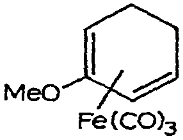
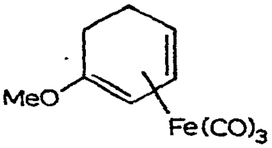
(continued)

^{13}NMR Chemical Shift Data *(continued)*

Compound	Solvent^a	$\delta(CO)^b$		References and remarks
		$\delta(CO)_{trans}$	$\delta(CO)_{cis}$	
$(\pi\text{-}C_5H_5)Fe(CO)_2Ph$	CH_2Cl_2	217.1		38
$(\pi\text{-}C_5H_5)Fe(CO)_2COPh$	CH_2Cl_2	215.1		38
$(\pi\text{-}C_5H_5)Fe(CO)_2CH_2Ph$	CH_2Cl_2	217.9		38
$[(\pi\text{-}C_5H_5)Fe(CO)(CNCH_2Ph)_2]Br$	$CHCl_3$	212.1		30
$(\pi\text{-}C_5H_5)Fe(CO)_2GePh_3$	CH_2Cl_2	216.3		38
$(\pi\text{-}C_5H_5)Fe(CO)_2SiPh_3$	CH_2Cl_2	216.5		38
$(\pi\text{-}C_5H_5)Fe(CO)_2SnPh_3$	CH_2Cl_2	215.7		38
$(\pi\text{-}C_4H_4)Fe(CO)_3$		208.6 ± 1		42
	CS_2/acetone 1/1	216.9 (area 1)	210.1 (area 2)	91, −78°
		208.4 ± 5		42
		211.3		43
		211.2		41
		214.8		60
$(\pi\text{-}C_8H_8)Fe(CO)_3$	$CF_2Cl_2/CHFCl_2$	211.7		47, −20°C
	$CF_2Cl_2/CHFCl_2$	212.4 (area 2)	210.3 (area 1)	−120°C
$Fe(CO)_2(NO)_2$	neat	206.6 ± 6		12,
$[(CO)_4FeCHO]Na$	THF	220.2		21
$(C_3F_7)Fe(CO)_4I$	$CHCl_3$	198.4		19
$(\pi\text{-}C_3H_6)Fe(CO)_3I$				
Two isomers {		209.9	206.8	52
		210.4	207.6	52
$[B_{10}H_{12}P]Fe(CO)_2(\pi\text{-}C_5H_5)$	CH_2Cl_2	207.8		55($J(^{31}P—^{13}C)$ 21.8 Hz)
$(CO)_3Fe(Me_2PCH_2CH_2PMe_2)$	C_6H_5Me	221.5		48($J(^{31}P—^{13}C)$ 6.9 Hz)
$[7,8\text{-}B_9H_{10}CHPFe(CO)_4^-]Me_4N^+$	CH_2Cl_2	213.3		44($J(^{31}P—^{13}C)$ 22 Hz)
$[HFe(CO)_4][Ph_3P{=}N{=}PPh_3]$	$CHCl_3$	209.3		55
$[Fe(CO)_3SMe]_2$	$CHCl_3$	209.0		19
$[HFe_3(CO)_{11}][Me_3NH]$	MeOH	222.6		55
$[(\pi\text{-}C_5H_5)Fe(CO)]_4$	CH_2Cl_2	289.8		55
	C_6F_6	217.4		68
	acetone	210.4		72

(continued)

^{13}NMR Chemical Shift Data *(continued)*

Compound	Solvent^a	δ(CO)^b		References and remarks
		δ(CO)$_{trans}$	δ(CO)$_{cis}$	
$(C_7H_8)Fe_2(CO)_6$	C_6H_6	215.0 (area 1)	212.7 (area 2)	79
	C_6H_6	211.7		79
	C_6H_6	213.0 (area 1)	211.4 (area 2)	79
	C_6H_6	211.9		79
	C_6H_6	211.4		79
	$CHCl_3$	201.0		82
	$CHCl_3$	201.7		82
(1,3-hexadiene)$Fe(CO)_3$	CS_2/acetone 1/1	212.7		91, −1°
		215.5 (area 1)	210.9 (area 2)	−93°
(cycloheptatriene)$Fe(CO)_3$	CS_2/acetone 1/1	211.7		91, −1°
		214.8 (area 1)	210.9 (area 2)	−73°
Ruthenium compounds				
$Ru_3(CO)_{12}$	$CHCl_3$	198.8 (area 1)	188.7 (area 1)	55

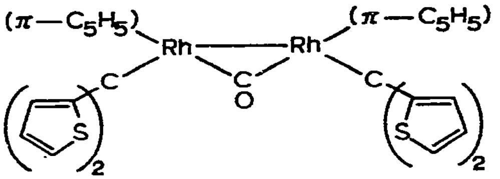
(continued)

^{13}NMR Chemical Shift Data *(continued)*

Compound	Solvent^a	$\delta(\mathrm{CO})^b$		References and remarks
		$\delta(\mathrm{CO})_{trans}$	$\delta(\mathrm{CO})_{cis}$	
cis-$\mathrm{RuCl_2(CO)_2(PEt_3)_2}$	$\mathrm{CH_2Cl_2}$	195.4		34 ($J(^{31}\mathrm{P}-^{13}\mathrm{C})$ 10.6 Hz)
cis-$\mathrm{RuCl_2(CO)_2(PEt_2\text{-}t\text{-}Bu)_2}$	$\mathrm{CH_2Cl_2}$	197.4		34 ($J(^{31}\mathrm{P}-^{13}\mathrm{C})$ 10.9 Hz)
cis-$\mathrm{RuCl_2(CO)_2(PMe\text{-}t\text{-}Bu_2)_2}$	$\mathrm{CH_2Cl_2}$	198.3		34 ($J(^{31}\mathrm{P}-^{13}\mathrm{C})$ 10.7 Hz)
cis-$\mathrm{RuCl_2(CO)_2(PEt_2Ph)_2}$	$\mathrm{CH_2Cl_2}$	193.9		34 ($J(^{31}\mathrm{P}-^{13}\mathrm{C})$ 11.0 Hz)
cis-$\mathrm{RuCl_2(CO)_2(P\text{-}n\text{-}Bu_2\text{-}t\text{-}Bu)_2}$	$\mathrm{CH_2Cl_2}$	197.3		34 ($J(^{31}\mathrm{P}-^{13}\mathrm{C})$ 11.0 Hz)
cis-$\mathrm{RuCl_2(CO)_2(PPh_2Et)_2}$	$\mathrm{CH_2Cl_2}$	193.7		34 ($J(^{31}\mathrm{P}-^{13}\mathrm{C})$ 10.6 Hz)
$\mathrm{H_3Ru_3(CO)_9CCH_3}$	$\mathrm{C_6H_6}$	190.1 (area 1)	189.3 (area 2)	54
$\mathrm{HRu_3(CO)_9C_6H_9}$		192.1, 198.5, 199.7	196.6, 199.3,	53
$\mathrm{(Ph_3P)_2Ru(CO)_3}$	$\mathrm{CH_2Cl_2}$	208.1		55 triplet ($J(^{31}\mathrm{P}-^{13}\mathrm{C})$ 17.1 Hz)
Osmium compounds				
cis-$\mathrm{OsCl_2(CO)_2(P\text{-}n\text{-}Pr_2\text{-}t\text{-}Bu)_2}$	$\mathrm{CH_2Cl_2}$	177.6		34 ($J(^{31}\mathrm{P}-^{13}\mathrm{C})$ 7.3 Hz)
$\mathrm{[Os(CO)NO(C_2H_4)(PPh_3)_2]PF_6}$		182.9		73 ($J(^{31}\mathrm{P}-^{13}\mathrm{C})$ 8 Hz)
Cobalt compounds				
$\mathrm{Co_2(CO)_8}$	$\mathrm{CH_2Cl_2}$	202.5		55, −20°C
$(\pi\text{-}\mathrm{C_5H_5)Co(CO)_2}$	THF	206.1		55
$\mathrm{[Co(CO)_4][Ph_3P{=}N{=}PPh_3]}$	$\mathrm{CH_2Cl_2}$	211.2		55, 56 ($J(^{59}\mathrm{Co}-^{13}\mathrm{C})$ 289 Hz)
$\mathrm{Hg[Co(CO)_4]_2}$	$\mathrm{CH_2Cl_2}$	201.6		55
	THF	203.1		55
$\mathrm{Co_3(CO)_9CBr}$	$\mathrm{CHCl_3}$	186.2		30
$\mathrm{(OC)_9Co_3CCH_2OH}$	$\mathrm{CHCl_3}$	200.6		83
$\mathrm{[(OC)_9Co_3CCH_2]HSO_4}$	$\mathrm{H_2SO_4}$	192.7		83
$\mathrm{(OC)_9Co_3CCH(CH_3)OH}$	$\mathrm{CHCl_3}$	200.5		83
$\mathrm{[(OC)_9Co_3CCH(CH_3)]HSO_4}$	$\mathrm{H_2SO_4}$	193.2		83
$\mathrm{(OC)_9Co_3CCH(C_6H_5)OH}$	$\mathrm{CHCl_3}$	200.2		83
$\mathrm{[(OC)_9Co_3CCH(C_6H_5)]HSO_4}$	$\mathrm{H_2SO_4}$	192.4		83
Rhodium compounds				
$\mathrm{Rh_4(CO)_{12}}$	$\mathrm{CHCl_3}$	190.3		18, 56°C, quintet ($J(^{103}\mathrm{Rh}-^{13}\mathrm{C})$ 17.1 Hz)
$\mathrm{Rh_4(CO)_{12}}$	$\mathrm{CH_2Cl_2}$			69, 78, −65°C
		183.4		triplet ($J(^{103}\mathrm{Rh}-^{13}\mathrm{C})$ 35 Hz)
		181.8		doublet ($J(^{103}\mathrm{Rh}-^{13}\mathrm{C})$ 75 Hz)
		175.5		doublet ($J(^{103}\mathrm{Rh}-^{13}\mathrm{C})$ 64 Hz)
				doublet ($J(^{103}\mathrm{Rh}-^{13}\mathrm{C})$ 62 Hz)
$(\pi\text{-}\mathrm{C_5H_5)Rh(CO)_2}$	$\mathrm{CHCl_3}$	190.9		35, 90 ($J(^{103}\mathrm{Rh}-^{13}\mathrm{C})$ 83.5 Hz)
	$\mathrm{CH_2Cl_2}$	193.2		55 ($J(^{103}\mathrm{Rh}-^{13}\mathrm{C})$ 83 Hz)
$[(\pi\text{-}\mathrm{C_5H_5)Rh(CO)]_2CO}$	$\mathrm{CH_2Cl_2}$	203.8		37, 25°C ($J(^{103}\mathrm{Rh}-^{13}\mathrm{C})$ 43 Hz)
	$\mathrm{CH_2Cl_2}$	231.8	(area 1)	37, −80° ($J(^{103}\mathrm{Rh}-^{13}\mathrm{C})$ 45 Hz
		191.8	(area 2)	($J(^{103}\mathrm{Rh}-^{13}\mathrm{C})$ 83 Hz)
$\mathrm{(pyridine)Rh(CO)_2Cl}$	$\mathrm{CH_2Cl_2}$	183.1		55 ($J(^{103}\mathrm{Rh}-^{13}\mathrm{C})$ 64.5 Hz)
		181.2		($J(^{103}\mathrm{Rh}-^{13}\mathrm{C})$ 67.3 Hz)
$\mathrm{(acac)Rh(CO)_2}$	$\mathrm{CH_2Cl_2}$	183.8		55 ($J(^{103}\mathrm{Rh}-^{13}\mathrm{C})$ 71.9 Hz)
$\mathrm{(Ph_3P)Rh(CO)\ (acac)}$	$\mathrm{CH_2Cl_2}$	189.5		55 ($J(^{103}\mathrm{Rh}-^{13}\mathrm{C})$ 74.8 Hz) ($J(^{31}\mathrm{P}-^{13}\mathrm{C})$ 24.8 Hz)
$\mathrm{(Ph_3As)Rh(CO)\ (acac)}$	$\mathrm{CH_2Cl_2}$	188.4		55 ($J(^{103}\mathrm{Rh}-^{13}\mathrm{C})$ 73.7 Hz)

(continued)

^{13}NMR Chemical Shift Data *(continued)*

Compound	Solvent[a]	δ(OC)[b]		References and remarks
		$\delta(CO)_{trans}$	$\delta(CO)_{cis}$	
$[(Et_2Ph)P]_2RhCl(CO)$	$CHCl_3$	179.8		55 ($J(^{103}Rh—^{13}C)$ 64.9 Hz) ($J(^{31}P—^{13}C)$ 9.6 Hz)
$[(o\text{-}MeC_6H_4)_3Sb]_2RhCl(CO)$	CH_2Cl_2	185.5		55 ($J(^{103}Rh—^{13}C)$ 68.3 Hz)
(phthalate)$Rh_2(CO)_4$	CH_2Cl_2	181.6		55 ($J(^{103}Rh—^{13}C)$ 72.7 Hz)
$[Rh(CO)_2Cl]_2$	CH_3CN	181.30		55 ($J(^{103}Rh—^{13}C)$ 71.9 Hz)
	C_6H_6	177.80		55 ($J(^{103}Rh—^{13}C)$ 77.5 Hz) 18 ($J(^{103}Rh—^{13}C)$ 68.8 Hz)
$[(C_5H_5N)RhCl(CPh_2)]_2CO$	CH_2Cl_2	206.5		28 triplet ($J(^{103}Rh—^{13}C)$ 47.3 Hz)
$[(\pi\text{-}C_5H_5)Rh(CPh_2)]_2CO$	CH_2Cl_2	223.4		28 triplet ($J(^{103}Rh—^{13}C)$ 42.4 Hz)
$(\pi\text{-}C_5H_5)_3Rh_3(CO)[(C_6F_5)_2C_2]$	CH_2Cl_2	217.8		49 triplet ($J(^{103}Rh—^{13}C)$ 48.5 Hz)
$(\pi\text{-}C_5H_5)_3Rh_3(CO)(Ph_2C_2)$	CH_2Cl_2	236.0		49, room temperature, quartet ($J(^{103}Rh—^{13}C)$ 38.7 Hz)
	CH_2Cl_2	241.6		49, —88°C, triplet of doublets ($J(^{103}Rh—^{13}C)$ 43.7 Hz) ($J(^{103}Rh—^{13}C)$ 28.4 Hz)
	CH_2Cl_2	221.1		55, triplet ($J(^{103}Rh—^{13}C)$ 41.4 Hz)
Iridium compounds				
$(\pi\text{-}C_5H_5)Ir(CO)_2$	THF	173.8		55
Nickel compounds				
$Ni(CO)_4$	neat	191.2		19, 92
	C_6H_6	191.6 ± 5		12,88
(diphos)$Ni(CO)_2$	$CHCl_3$	200.7		55
$(Ph_3P)_2Ni(CO)_2$	$CHCl_3$	199.4		55
$[(PhO)_3P]_2Ni(CO)_2$	DMF	195.6		55, triplet ($J(^{31}P—^{13}C)$ 3 Hz)
	$CHCl_3$	194.7		15
$[(\pi\text{-}C_5H_5)Ni(CO)]_2$	CH_2Cl_2	225.2		55

[a] No distinction will be made between deuterated and nondeuterated solvents. [b] Th = 2-thienyl group. [c] Fu = 2-furanyl group. [d] If values of δ(C) are reported in the same solvent in different papers and the results agree ± 0.5 ppm, an average value is listed. [e] The structure of the compound is not definitely known.

Acknowledgements

The authors are indebted to Mr. William Wright and Miss Kathy Norton for their capable assistance with the manuscript. Some of the research was supported by the National Science Foundation under Grant GP-33267X.

References

1 J.B. Stothers, Carbon-13 NMR Spectroscopy, Academic Press, New York, 1972.
2 F. Basolo and R.G. Pearson, Mechanisms of Inorganic Reactions, 2nd ed., Wiley, New York, 1967.
3 F. Basolo, Chem. Brit., 5 (1969) 505.
4 R.D.W. Kemmitt and J. Burgess, Inorg. React. Mech. (Specialist Period. Rep. J. Chem. Soc.), 1 (1971) 265.
5 R.D.W. Kemmitt and J. Burgess, Inorg React. Mech. (Specialist Period. Rep. J. Chem. Soc.), 2 (1972) 247.
6 H. Werner, Angew. Chem., Internat. Edit., 7 (1968) 930.
7 D.A. Brown, Inorg. Chim. Acta Rev., 1 (1967) 35.
8 R.J. Angelici, Organometal. Chem. Rev., 3 (1968) 173.
9 G. Reichenbach. J. Organometal. Chem., 31 (1971) 103.
10 J.R. Wilkinson, T. Yamamoto and L.J. Todd, unpublished results.
11 F.A. Cotton, A. Danti, J.S. Waugh and R.W. Fessenden, J. Chem. Phys., 29 (1958) 1427.
12 R. Bramely, B.N. Figgis and R.S. Nyholm, Trans. Faraday Soc., 58 (1962) 1893.
13 B.E. Mann, J. Chem. Soc., Chem. Commun., (1971) 1173.
14.J.P. Jesson and P. Meakin, J. Amer Chem. Soc., 95 (1973) 1344.
15 G.M. Bodner and L.J. Todd, Inorg. Chem., 13 (1974) 1335
16 O.A. Gansow, A.R. Burke and W.D. Vernon, J. Amer. Chem. Soc., 94 (1972) 2550.
17 O.A. Gansow, B.Y. Kimura, G.R. Dobson and R.A. Brown, J. Amer. Chem. Soc., 93 (1971) 5922.
18 F.A. Cotton, L. Kruczynski, B.L. Shapiro and L.F. Johnson, J. Amer. Chem. Soc., 94 (1972) 6191.
19 P.C. Lauterbur and R.B. King, J. Amer. Chem. Soc., 87 (1965) 3266.
20 P.S. Braterman, D.W. Milne, E.W. Randall and E. Rosenberg, J.Chem. Soc. Dalton, (1973) 1027.
21 J.P. Collman and S.R. Winter, J. Amer. Chem. Soc., 95 (1973) 4089.
22 J.A Connor, E.M. Jones, E.W. Randall and E. Rosenberg, J. Chem. Soc., Dalton, (1972) 2419.
23 G.M. Bodner, S.B. Kahl, K. Bork, B.N. Storhoff, J.E. Wuller and L.J. Todd, Inorg. Chem., 12 (1973) 1071.
24 D.J. Ciappenelli, F.A. Cotton and L. Kruczynski, J. Organometal. Chem., 50 (1973) 171.
25 C.G. Kreiter and V. Formacek, Angew. Chem. Int. Ed., 11 (1972) 141.
26 F.R. Kreissl, E.O. Fischer, C.G. Kreiter and K. Weiss, Angew. Chem. Int. Ed., 12 (1973) 563
27 F.R. Kreissl, E.O. Fischer, C.G. Kreiter and H. Fischer, Chem. Ber., 106 (1973) 1262.
28 T. Yamamoto, A.R. Garber, J.R. Wilkinson, C.B. Boss, W.E. Streib and L.J. Todd, J. Chem. Soc., Chem. Commun., (1974) 354.
29 E.O. Fischer, G. Kreis and F.R. Kreissl, J. Organometal. Chem., 56 (1973) C37.
30 L.F. Farnell, E.W. Randell and E. Rosenberg, J. Chem. Soc., Chem. Commun., (1971) 1078.
31 J.W. Wilson and E.O. Fischer, J. Organometal. Chem., 57 (1973) C63.
32 E.O. Fischer. G. Kreis, C.G. Kreiter, J. Müller, G. Huttner and H. Lorenz, Angew. Chem. Int. Ed., 12 (1973) 564.
33 O.A. Gansow and B.Y. Kimura, J. Chem. Soc., Chem. Commun., (1970) 1621.
34 D.F. Gill, B.E. Mann and B.L. Shaw, J. Chem. Soc., Dalton, (1973) 311.
35 D.E. Axelson, C.E. Holloway and A.J. Oliver, Inorg. Nucl. Chem. Lett., 9 (1973) 885.
36 O.A. Gansow, A.R. Burke and G.N. LaMar, J. Chem. Soc., Chem. Commun., (1972) 456.
37 J. Evans, B.F.G. Johnson, J. Lewis and J.R. Norton, J. Chem. Soc., Chem. Commun., (1973) 79.
38 O.A. Gansow, D.A. Schexnayder and B.Y. Kimura, J. Amer. Chem. Soc., 94 (1972) 3406.
39 B.E. Mann, J. Chem. Soc., Chem. Commun., (1971) 976.
40 E.W. Randall, personal communication.
41 G.F. Emerson, K. Ehrlich, W.P. Giering and P.C. Lauterbur, J. Amer. Chem. Soc., 88 (1966) 3172.
42 H.G. Preston, Jr. and J.C. Davis, Jr., J. Amer Chem. Soc., 88 (1966) 1585.
43 H. Retcotsky, E.N. Frankel and H.S. Gutowsky, J. Amer Chem. Soc., 88 (1966) 2710.
44 D.C. Beer and L.J. Todd, J. Organometal. Chem., 55 (1973) 363.
45 C.G. Kreiter and M. Lang, J. Organometal. Chem., 55 (1973) C27.
46 F.R. Kreissl, E.O. Fischer and C.G. Kreiter, J. Organometal. Chem., 57 (1973) C9.
47 G. Rigatti, G. Boccalon, A. Ceccon and G. Giacommeti, J. Chem. Soc., Chem. Commun., (1972) 1165.
48 M. Akhtar, P.D. Ellis, A.G. MacDiarmid and J.D. Odom, Inorg. Chem., 11 (1972) 2917.
49 T. Yamamoto, A.R. Garber, G.M. Bodner and L.J. Todd, J. Organometal. Chem., 56 (1973) C23.
50 K. Noack and M. Ruch, J. Organometal. Chem., 17 (1969) 309.
51 R.D. Adams and F.A. Cotton, Inorg Chim. Acta, 7 (1973) 153.
52 E.W. Randall, E. Rosenberg, and L. Milone, J. Chem. Soc., Dalton, (1973) 1672.
53 M. Evans, M. Hursthouse, E.W. Randall, E. Rosenberg, L. Milone and M. Valle, J. Chem. Soc., Chem. Commun., (1972) 545.

54 A.J. Canty, B.F.G. Johnson, J. Lewis and J.R. Norton, J. Chem. Soc., Chem. Commun., (1972) 1331.
55 J.R. Wilkinson, A.R. Garber and L.J. Todd, unpublished data.
56 E.A.C. Lucken. K. Noack and D.F. Williams, J. Chem. Soc., A, (1967) 148.
57 F. Calderazzo, E.A.C. Lucken and D.F. Williams, J.Chem. Soc., A, (1967) 154.
58 L.J. Todd, Pure Appl. Chem., 30 (1972) 587.
59 D.C. Beer and L.J. Todd, J. Organometal. Chem., 36 (1972) 77.
60 W.E. Billups, L.P. Lin and O.A. Gansow, Angew. Chem. Int. Ed., 11 (1972) 637.
61 D.J. Ciappenelli, F.A. Cotton and L. Krucznski, J. Organometal. Chem., 42 (1972) 159.
62 G.C. Levy and G.L. Nelson, Carbon-13 Nuclear Magnetic Resonance for Organic Chemists, Wiley-Interscience New York, 1972.
63 D.F. Keeley and R.E. Johnson, J.Inorg. Nucl. Chem., 11 (1959) 33.
64 J.P. Collman, J.N. Cawse and J.I. Brauman, J.Amer. Chem. Soc., 94 (1972) 5905.
65 J.A. Pople, Mol. Phys., 7 (1964) 301.
66 J.G. Bullitt, F.A. Cotton and T.J. Marks, J. Amer. Chem. Soc., 92 (1970) 2155.
67 R.M. Kirshner, T J. Marks, J.S. Kristoff and J.A. Ibers, J.Amer. Chem. Soc., 95 (1973) 6602.
68 D.J. Cardin, B. Cetinkaya, E. Cetinkaya, M.F. Lappert, E.W. Randall and E. Rosenberg, J. Chem. Soc., Dalton, (1973) 1982.
69 J. Evans, B.F.G. Johnson, J. Lewis, J.R. Norton and F.A. Cotton, J Chem. Soc., Chem. Commun., (1973) 807.
70 T.A. George and D.C. Turnipseed, Inorg. Chem., 12 (1973) 394.
71 B.E. Mann, J. Chem. Soc., Dalton, (1973) 2012.
72 J. Evans, D.V. Howe, B.F.G. Johnson and J. Lewis, J. Organometal. Chem., 61 (1973) C48.
73 B.F.G. Johnson and J.A. Segal, J. Chem. Soc., Chem. Commun., (1972) 1312.
74 E.O. Fischer, K.R. Schmid, W. Kalbfus and C.G Kreiter, Chem. Ber., 106 (1973) 3893.
75 E.O. Fischer, G. Kreis, F.R. Kreissl, C.G. Kreiter and J. Muller, Chem. Ber., 106 (1973) 3910.
76 P.V. Petrovskii, E I. Fedin, L.A. Fedorov, A.G. Ginzburg, V N. Setkina and D.N. Kursanov, Dokl. Akad. Nauk SSSR, 210 (1973) 605.
77 T.A. George, personal communication.
78 B.F.G. Johnson, personal communication.
79 G. Deganello, J. Organometal. Chem., 59 (1973) 329.
80 F A. Cotton, B.G. DeBoer and T.J. Marks, J. Amer. Chem. Soc , 93 (1971) 5069.
81 E. Rosenberg, D. Harris and J.D. Roberts, Abstr. 6th Internal. Conf. Organometal. Chem., Amherst. Mass., August 1973 (No. 256).
82 R.E. Ireland, G.G. Brown, Jr., R.H. Stanford, Jr. and T.C. McKenzie, J.Org. Chem., 39 (1974) 51.
83 D. Seyferth, G.H. Williams and D.D. Traficante, J. Amer. Chem. Soc., 96 (1974) 604.
84 T.C. Farrar and E.D. Becker, Pulse and Fourier Transform NMR, Academic Press, New York, 1971.
85 K. Noack, Helv. Chim. Acta, 47 (1964) 1064.
86 G. Bor, Spectrochim. Acta, 19 (1963) 2065.
87 E.R. Corey and L.F. Dahl, Inorg. Chem., 1 (1962) 521.
88 R. Bramely, B.N. Figgis and R.S. Nyholm. J. Chem. Soc., A, (1967) 861.
89 O.A. Gansow, A.R. Burke and W.D. Vernon, Abstr. 164th Amer. Chem. Soc. Meeting, New York, August, 1972, INOR-108.
90 D.E. Axelson, personal communication.
91 L. Kruczynski and J. Takats, J. Amer. Chem. Soc., 96 (1974) 932.
92 J B. Stothers and P.C. Lauterbur, Can. J. Chem., 42 (1964) 1563

Note added in proof

A review article containing metal carbonyl chemical shift and coupling constant information has appeared recently (B.E. Mann, Advan. Organometal. Chem., 12 (1974) 135).

Information on some platinum carbonyl compounds has been reported (M.H. Chisholm, H.C. Clark, L.E. Manzer, J.B. Stothers and J.E.H. Ward, J. Amer. Chem. Soc., 95 (1973) 8574). The chemical shift values are at high field (159-177 ppm) as expected (see Fig. 3).

It should be noted that the trends outlined in Section IVA do not apply for certain one-electron ligands. The *trans*-carbonyl resonance of $Re_2(CO)_{10}$ (see Section V) is at higher field than the *cis*-carbonyl resonance. The observed carbonyl resonance of $(C_3F_7)Fe(CO)_4I$ is also at an unusual high field position.