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A CARBON-13 NMR STUDY OF SOME PENTACARBONYLRHENIUM COMPLEXES

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Summary

Carbon-13 NMR data are reported for derivatives $XRe(CO)_5$ ($X = CH_3$, CH_3CO, C_6H_5, C_6H_5CO, Br, Cl_3Si, Me_3Si, Me_3Ge, Me_3Sn, Me_3Pb). Spectra of good quality were obtained at ambient temperature except for $X = Me_3Pb$. In the $XRe(CO)_5$ series, the carbonyl carbon *trans* to X is more shielded (resonance at higher field) than carbonyl carbons cis to X. However, in the cationic complex $[CH_3CNRe(CO)_5][PF_6]$, the carbonyl carbon *trans* to CH_3CN is less shielded than those in *cis* positions. Although there is a linear relation between the ^{13}C chemical shift and the stretching force constant for *cis* carbonyls in the $XRe(CO)_5$ series, there is no apparent correlation of force constants with other features of the ^{13}C NMR spectra.

Introduction

Over the past several years the quantity of ^{13}C NMR data for transition metal carbonyl complexes has increased rapidly. An excellent recent review by Todd and Wilkinson [1] is a useful guide to the results published to date and the conclusions drawn therefrom, and it is clear that little attention has so far been paid to carbonyl derivatives of the Group VII transition metals. The nuclei ^{55}Mn, ^{185}Re and ^{187}Re, all with $I = 5/2$, possess quadrupole moments which can potentially broaden the signals of carbon atoms bound directly to them. Carbonyl carbon resonances in manganese carbonyl derivatives are typically broad [1] and, possibly because of expectations of similar behaviour in the case of rhenium, only two rhenium carbonyl complexes have been investigated prior to this work, namely $Re_2(CO)_{10}$ and $BrRe(CO)_5$. These compounds were recently reported by Todd and Wilkinson [2] to give "fairly well resolved" spectra at ambient temperatures in THF. These authors have also demonstrated that resonances broadened by coupling to quadrupolar transition metal nuclei can be significantly sharpened by sufficiently cooling the samples [2].

In our recent work with carbene derivatives of manganese and rhenium [3, 4], ^{13}C NMR proved to be a valuable tool in assigning structures to these complexes. In view of the high quality of spectra obtained for rhenium complexes of direct interest to us [5], we have studied a wider range of rhenium carbonyl derivatives. In this paper we present results for an extensive series of neutral mono-substituted rhenium pentacarbonyl complexes, $XRe(CO)_5$, plus one derivative of the type $[LRe(CO)_5]^+PF_6^-$ ($L = CH_3CN$)*. Most of the neutral complexes gave sharply resolved spectra at ambient temperatures in $CDCl_3$, and an excellent spectrum of the salt was obtained at ambient temperature in CD_3CN. In the case of two neutral derivatives studied at high temperatures in toluene-d_8, resonances due to inequivalent carbonyl carbon atoms were still clearly resolvable at 100°C. The ^{13}C NMR chemical shifts are discussed in terms of their correlation with Cotton—Kraihanzel (CK) carbonyl stretching force constants and the limitations of this often-used treatment are pointed out.

Results and discussion

(1). Neutral complexes of the type $XRe(CO)_5$

Recently it has been shown that ^{13}C NMR spectra of carbonyl derivatives of transition metals with nuclear quadrupole moments can be obtained by the method of "temperature relaxation" [2]. In our own studies of rhenium carbonyl derivatives we have found quadrupole broadening not to be a problem in most cases. Satisfactory spectra can usually be obtained at ambient temperatures in $CDCl_3$ (see Table 1). Difficulties have been encountered only with $Re_2(CO)_{10}$, which gave one broad signal at ca. −191.2 ppm relative to TMS, presumably due to the eight equivalent equatorial carbonyl carbon atoms, and $(CH_3)_3PbRe(CO)_5$ for which a broad, unresolved signal in the carbonyl region at ca. −189.3 ppm was observed. In the case of $ClRe(CO)_5$ there were severe solubility limitations in $CDCl_3$ and after several thousand pulses no carbonyl resonances were observed.

The ^{13}C NMR results will now be discussed under two headings: (a) resonances due to carbon atoms other than carbonyl carbons atoms, and (b) resonances due to carbonyl carbon atoms.

(a) Resonances due to carbon atoms other than carbonyl carbon atoms. Few examples of ^{13}C NMR chemical shifts for acyl carbon atoms bound to transition metals have been reported. The values of −245.4 and −244.0 ppm found for $C_6H_5CORe(CO)_5$ and $CH_3CORe(CO)_5$ (Fig. 1) are shifted upfield with respect to the iron derivative $(\eta\text{-}C_5H_5)Fe(CO)_2COCH_3$ for which the chemical shift of the acyl carbon atom is −254.4 ppm [6]. It would therefore be of interest to obtain the spectra of $C_6H_5COMn(CO)_5$ and $CH_3COMn(CO)_5$ to compare closely related compounds within one transition metal group.

The molecule $C_6H_5Re(CO)_5$ represents one of the few reports of phenyl

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[*] In the discussion of these rhenium derivatives and related complexes, the symbol L will refer to neutral two-electron donor ligands such as phosphines or acetonitrile, and X will refer to ligands which may formally be described as neutral one-electron donors or anionic two-electron donors, e.g. $(CH_3)_3Si$, Br, CH_3.

TABLE 1

^{13}C NMR DATA FOR PENTACARBONYLRHENIUM COMPLEXES [a]

Compound	δ(CO) (*cis*)	δ(CO) (*trans*)	Line width [b]	Other δ (assignment) [coupling constants]
$Cl_3SiRe(CO)_5$	−180.5	−178.5	11	
$(CH_3)_3SiRe(CO)_5$	−187.9	−182.9	9	−6.6 (CH_3)
$(CH_3)_3GeRe(CO)_5$	−187.5	−182.7	10	−4.9 (CH_3)
$(CH_3)_3SnRe(CO)_5$	−187.7	−182.9	13	+7.5 (CH_3); [$^1J(^{117}Sn-^{13}C)$ = 241 Hz; $^1J(^{119}Sn-^{13}C)$ = 252 Hz]
$(CH_3)_3PbRe(CO)_5$	ca. −189.3 [c]			+5.0 (CH_3); [$^1J(^{207}Pb-^{13}C)$ = 88 Hz]
$CH_3Re(CO)_5$	−185.2	−181.3	8	+38.0 (CH_3)
$C_6H_5Re(CO)_5$	−183.6	−181.7	4	−145.5 (*o*- or *m*-); −134.4 (carbon bound to Re); −128.7 (*m*- or *o*-); −124.3 (*p*-)
$CH_3CORe(CO)_5$	−183.0	−181.2	7	−244.0 (C=O); −57.2 (CH_3)
$C_6H_5CORe(CO)_5$	−182.9	−181.0	6	−245.4 (C=O); −154.6 ($\underline{C}$-CO); −130.8 (*p*-); −128.3 (*o*- or *m*-); −126.2 (*m*- or *o*-)
$BrRe(CO)_5$ [d]	−177.8	−176.3	10	
$[(CH_3CN)Re(CO)_5][PF_6]$ [e]	−178.6	−179.6	6	−128.1 (CN); −4.3 (CH_3)

[a] Chemical shifts in ppm relative to tetramethylsilane; $CDCl_3$ solvent except as noted. [b] Line width at half height in Hz for *cis* carbonyl signal. [c] See text. [d] Spectrum of lower quality due to low solubility; lower precision in δ(CO) (*trans*). [e] CD_3CN solvent.

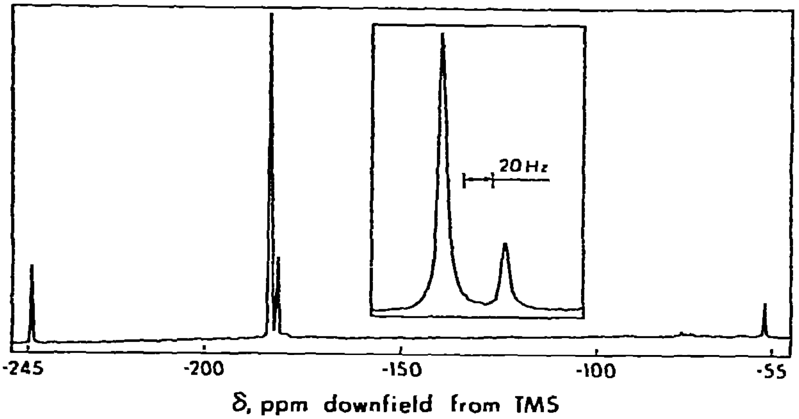

Fig. 1. ${}^{13}C$ NMR spectrum of $CH_3CORe(CO)_5$, in $CDCl_3$ at ambient temperature, showing an expansion of the carbonyl region as well as the full spectrum. This was one of the most concentrated solutions studied (>1.0 *M*) and the solvent resonance appears as a very weak triplet at −77.035 on the above scale, it could still be employed as the internal reference, however.

carbon resonances due to a phenyl group σ-bonded to a transition metal, other examples being $(\eta\text{-}C_5H_5)_2TiPh_2$, *cis*-$[PtPh_2(PEt_3)_2]$, *trans*-$[PtPh_2(PEt_3)_2]$ and $[PtPh_2Cl_2(PEt_3)_2]$ [7]. Carbonyl resonances for the complexes $(\eta\text{-}C_5H_5)Fe(CO)_2X$ ($X = C_6H_5$, *p*-C_6H_4Cl, C_6F_5) have been reported [8], but the phenyl carbon resonances were omitted. Phenyl resonances for $C_6H_5Re(CO)_5$ and $C_6H_5CORe(CO)_5$ could be assigned on a relative intensity basis, the weakest signal being due to the carbon atom bound to rhenium (this carbon atom has no hydrogen atom attached to it and does not benefit from Overhauser enhancement in a proton-decoupled spectrum). The *para*-carbon signal is of intermediate intensity and the two pairs of *ortho*- and *meta*-carbons give the strongest signals. The phenyl resonances in $C_6H_5CORe(CO)_5$ were similarly assigned and are also listed in Table 1. These assignments were confirmed using proton coupled spectra. All of the phenyl carbon resonances showed small long range couplings to hydrogen atoms on the phenyl ring, but carbon atoms directly bound to hydrogen were in addition split into widely separated doublets [${}^1J({}^1H\text{—}{}^{13}C)$ values were of the order of 160 Hz].

The resonance of the methyl carbon in $CH_3Re(CO)_5$ lies to high field of TMS at +38.0 ppm. It is also more highly shielded than that in $CH_3Mn(CO)_5$ which occurs at +212.2 ppm relative to CS_2 [9] (+19.4 ppm relative to TMS), and is in fact the highest field resonance of this type yet reported [7]. The most highly shielded example previously observed was the methyl carbon resonance of $(\eta\text{-}C_5H_5)W(CO)_3CH_3$ which occurs at +28.9 ppm [6].

In the complexes $(CH_3)_3SnRe(CO)_5$ and $(CH_3)_3PbRe(CO)_5$ couplings from the Group IV atoms to the methyl carbon atoms were observed. In the former case, even though an excellent spectrum of the carbonyl region was obtained, tin coupling to carbonyl carbon atoms was not observed. The coupling constants noted in Table 1 are rather similar to values found in this laboratory for the complexes *cis*-$Ru(CO)_4[Sn(CH_3)_3]_2$ and *cis*-$Ru(CO)_4[Pb(CH_3)_3]_2$ [10].

(b) Resonances due to carbonyl carbon atoms. Most of the complexes studied gave satisfactory spectra in the carbonyl region at ambient temperatures

(see Table 1); $(CH_3)_3PbRe(CO)_5$ was a notable exception. Even at −20°C in toluene-d_8 only a broad singlet (half width ca. 25 Hz) was observed and this became even broader at temperatures up to 70°C. The large half-width value over the wide temperature range employed suggests that quadrupole broadening and not stereochemical nonrigidity produces the observed line broadening. It therefore appears that lower temperatures will have to be employed to obtain a satisfactory spectrum of this complex. This behaviour can be contrasted with that of $(CH_3)_3GeRe(CO)_5$ and $CH_3Re(CO)_5$, in which the carbonyl peaks remain clearly resolved at elevated temperatures. Line widths observed for the carbonyls *cis* to the substituents in these complexes are 14 and 11 Hz respectively in toluene-d_8 at 100°C. Thus quadrupole broadening is not a serious problem for these complexes.

A great deal of the discussion of ^{13}C NMR chemical shift values for carbonyl carbon atoms has centered around their correlation with CK carbonyl stretching force constants [1]. In attempting a similar treatment of our own results, several interesting features have been noted.

In the following discussion of neutral mono-substituted metal carbonyl derivatives of the types $LM(CO)_5$, (M = Cr, W), and $XRe(CO)_5$, the four equivalent carbonyl ligands *cis* to L or X and the unique carbonyl group *trans* to L or X will be designated "*cis*" and "*trans*" respectively. The assignment of *cis* and *trans* carbonyl resonances in these systems is straightforward on the basis of relative peak intensities.

For the neutral monosubstituted rhenium carbonyl derivatives listed in Table 1 it can be seen that the *trans* carbonyl resonance is upfield from (i.e., more shielded than) the *cis* carbonyl resonance. This phenomenon has been confirmed elsewhere for two rhenium derivatives [2] and has also been observed for a related manganese complex [2]. In contrast, complexes of the type $LW(CO)_5$ [11, 12] and $LCr(CO)_5$ [12, 13] give spectra in which the *trans* carbonyl resonance is always down-field from (i.e., more deshielded than) the *cis* carbonyl resonance. The significance of this reversal of shielding of *cis* and *trans* carbonyls is apparent when it is considered that the force constant of the *trans* carbonyl is always lower than that of the *cis**. Thus it follows that in a given molecule one can make no prediction as to whether the *cis* or *trans* carbonyl will be more shielded on the basis of CK carbonyl stretching force constants.

In complexes of the type *cis*-$X_2M(CO)_4$, where X is H [16] or a Group IV ligand [10], and M = Fe, Ru, Os, the resonances of carbonyl atoms *trans* to X are also found to be more shielded than those of the *cis* carbonyl carbons.

Little work has been done on mono-substituted derivatives of manganese pentacarbonyl. However, it does appear that the generally observed [1] large increase in shielding of carbonyl carbon resonances upon descending a transition metal group is in evidence here. The ^{13}C NMR spectrum of $CH_3Mn(CO)_5$ in the carbonyl region exhibits a broad, unresolved singlet at −21 ppm relative to

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* In octahedral complexes of this type $k_1 < k_2$ in all known instances. Previous force constant values for $Ph_3GeMn(CO)_5$ and $Ph_3SnMn(CO)_5$ [14] are incorrect due to a wrong assignment. Correct energy factored values for $Ph_3GeMn(CO)_5$ are k_1 = 16.40, k_2 = 16.71, while those for $Ph_3SnMn(CO)_5$ are 16.34 and 16.66 mdyn/Å [15]. These compounds are thus not exceptions to the generalization that $k_1 < k_2$.

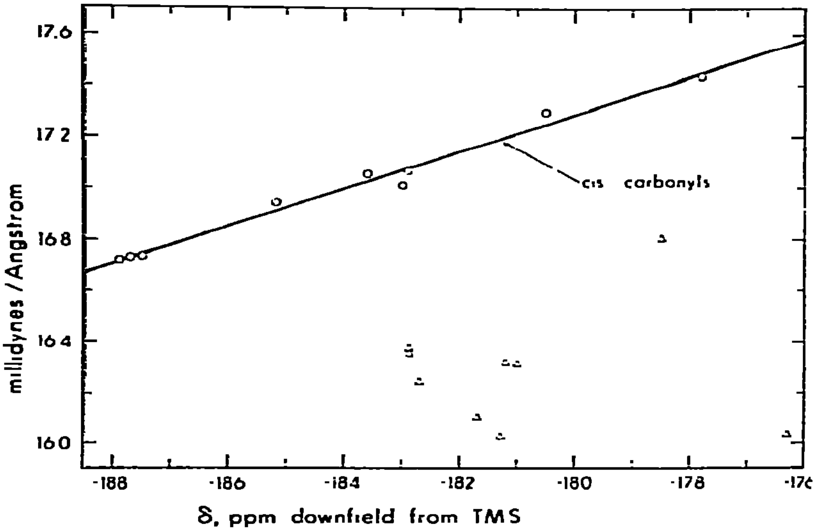

Fig. 2. Cotton—Kraihanzel carbonyl stretching force constants versus ^{13}C chemical shifts for $XRe(CO)_5$ complexes. O, carbonyls *cis* to X; Δ, carbonyls *trans* to X.

CS_2 [9] (−214 ppm relative to TMS), and that of $C_6H_5CH_2Mn(CO)_5$ at −87°C shows two signals at −211.1 and −209.1 ppm due to *cis* and *trans* carbonyls respectively [2]. These values can be compared with those of −185.2 and −181.3 ppm for the *cis* and *trans* carbonyls of $CH_3Re(CO)_5$. As has been mentioned previously [11, 12] such a large up-field shift when descending a group cannot be explained in terms of carbonyl stretching force constants.

To apply the usual treatment of experimental data to our own results a plot of Cotton—Kraihanzel carbonyl stretching force constants vs. ^{13}C chemical shifts is shown in Fig. 2. It can immediately be seen that for the *cis* carbonyl atoms an excellent correlation exists, with more highly shielded carbonyl carbon atoms belonging to ligands of higher force constants. It should be noted in this connection that points reported [11] for the *cis* carbonyls of complexes $LW(CO)_5$ fall on a continuation of the same straight line. However, the correlation for the *trans* carbonyl groups is poor, a phenomenon which has previously been noted for a series of carbene derivatives of chromium carbonyl [12]. Thus changing chemical shifts of *trans* carbonyl carbon atoms are not always reflected by changes in carbonyl force constants.

(2) *The ionic complex* $[(CH_3CN)Re(CO)_5][PF_6]$

A good spectrum of this compound was obtained at ambient temperature in CD_3CN solvent (see Table 1). The data will be discussed in terms of non-carbonyl and carbonyl atoms as before.

(a) Resonances due to carbon atoms other than carbonyl carbon atoms. Peaks due to cyanide carbon were observed at −128.1 and −118.3 ppm, and these were assigned to coordinated CH_3CN and to CD_3CN solvent, respectively. The absence of solvent exchange at ambient temperature was confirmed by a further experiment in which a small amount of CH_3CN was added to the solution. As well as the septet due to the CD_3 carbon of CD_3CN, two CH_3

TABLE 2

CARBONYL STRETCHING FREQUENCIES AND COTTON—KRAIHANZEL FORCE CONSTANTS FOR PENTACARBONYLRHENIUM COMPLEXES

Compound	Stretching frequencies [a] (cm^{-1})			Cotton—Kraihanzel force constants [b] (mdyn/Å)		
	$A_1^{(2)}$	E	$A_1^{(1)}$	k_1	k_2	k_i
$Cl_3SiRe(CO)_5$ [c]	2140	2038	2030	16.80	17.30	0.26
$(CH_3)_3SiRe(CO)_5$ [c]	2112	2001	2001	16.36	16.72	0.28
$(CH_3)_3GeRe(CO)_5$	2111	2002	1995	16.24	16.73	0.27
$(CH_3)_3SnRe(CO)_5$ [d]	2108	2003	2003	16.38	16.73	0.26
$(CH_3)_3PbRe(CO)_5$	2106	2003	1994	16.22	16.72	0.26
$CH_3Re(CO)_5$	2125	2013	1983	16.03	16.94	0.29
$C_6H_5Re(CO)_5$	2131	2020	1988	16.11	17.05	0.29
$CH_3CORe(CO)_5$	2131	2017	2000	16.32	17.01	0.29
$C_6H_5CORe(CO)_5$	2133	2021 [e]	2000	16.31	17.07	0.29
$BrRe(CO)_5$ [f]	2151	2044	1985	16.03	17.44	0.28
$[(CH_3CN)Re(CO)_5][PF_6]$	2170	2066	2031	16.80	17.79	0.27

[a] All spectra recorded in cyclohexane, except $[(CH_3CN)Re(CO)_5]^+PF_6^-$ in CH_2Cl_2. [b] k_1 = force constant of *trans* carbonyl. k_2 = force constant of *cis* carbonyls. [c] Stretching frequencies taken from ref. 21. [d] Stretching frequencies taken from ref. 18. [e] E mode split into two peaks of nearly equal intensity at 2025 and 2017 cm^{-1}. Mean value used in calculations. [f] Stretching frequencies taken from ref. 22.

singlets were observed at —4.3 and —1.6 ppm. The former resonance was that of the complexed CH_3CN group, the latter that of the free CH_3CN in solution. The spectrum was essentially unchanged at 70°C. Hence any exchange between the two is slow on the NMR time scale.

(b) Resonances due to carbonyl carbon atoms. It is interesting to note that the *trans* carbonyl resonance is downfield from the *cis* resonance in this case (see Table 1), in contrast to all the neutral rhenium derivatives discussed earlier. In this sense the spectrum resembles those of neutral complexes of the type $LM(CO)_5$ (M = Cr, Mo, W) where in all cases reported so far, the *trans* resonance is downfield from the *cis* [1]. The reason why the $[CH_3CNRe(CO)_5]^+$ salt shows such different behaviour from the neutral $XRe(CO)_5$ species is not clearly understood at present. However, it is important to note that the reversal cannot be explained in terms of force constants since the *cis* carbonyl force constants are higher than those of the *trans* carbonyl in all cases (see Table 2).

As can be readily seen the data for the *cis* carbonyl force constant and chemical shift will not produce a point on the straight line in Fig. 2. The significance of this is hard to interpret at the moment since changes in the solvents used for IR and NMR studies relative to the neutral $XRe(CO)_5$ derivatives may be at least partly responsible. It should also be noted here that the carbonyl resonances for $[CH_3CNRe(CO)_5]^+PF_6^-$ remain well resolved in CD_3CN at 70°C. In view of the interesting features observed for this compound we plan to study further cationic rhenium species of the type $[LRe(CO)_5]^+$.

Experimental

Compounds were prepared according to the methods in the references indicated: $CH_3Re(CO)_5$, $CH_3CORe(CO)_5$, $C_6H_5Re(CO)_5$ and $C_6H_5CORe(CO)_5$

were prepared by the method of Hieber et al. [17]. The sodium salt of $Re_2(CO)_{10}$ was used.

Displacement reactions using $Na^+Re(CO)_5^-$ were used in the preparation of $(CH_3)_3GeRe(CO)_5$, $(CH_3)_3SnRe(CO)_5$ [18], and $(CH_3)_3PbRe(CO)_5$. Details of the synthesis and characterization of the germanium compound will be presented elsewhere. The preparation of the lead compound has very recently been reported [19] and the infrared bands are in excellent agreement; we find the compound to be colorless, however. Samples of $Cl_3SiRe(CO)_5$ [20] and $(CH_3)_3SiRe(CO)_5$ [21] prepared by the reaction of $Re_2(CO)_{10}$ with Cl_3SiH and $(CH_3)_3SiH$ were kindly supplied by Dr. W. Jetz. The method of Kaesz et al. [22] was used in the preparation of $BrRe(CO)_5$ and $ClRe(CO)_5$; a sample of the former was supplied by Dr. D. Dong.

^{13}C NMR spectra were recorded using the Fourier transform pulsed NMR technique. Proton decoupling was employed in complexes containing hydrogen atoms except as noted in the discussion. Varian HA-100 and Bruker HFX-90 spectrometers were used, operating at 25.15 and 22.6 MHz respectively. The number of scans was typically in the range 1000 to 4000, the delay between scans of the order of 0.4 to 0.8 seconds, and the flip angle was approximately 45°. No relaxation reagent was used in any spectrum. Spectra of neutral complexes were recorded in $CDCl_3$ at ambient temperatures (45°C for the Varian HA-100, 35°C for the Bruker HFX-90), except as noted in the text. The salt $[CH_3CNRe(CO)_5][PF_6]$ was prepared as described by Okamoto [23] from $Re_2(CO)_{10}$ and $NOPF_6$ in CH_3CN solvent, and its spectrum was recorded in CD_3CN. Solution concentrations were generally of the order of 0.5 *M*, although somewhat higher in a few cases. ^{13}C chemical shifts were measured relative to the internal solvent resonance and are reported relative to TMS by use of the relations $\delta(TMS) = \delta(CDCl_3) - 77.035$ ppm and $\delta(TMS) = \delta(\underline{C}D_3CN) - 1.187$ ppm. The sign convention employed gave carbon atoms deshielded with respect to TMS negative δ values. In cases where several spectra of a particular complex were obtained, chemical shift values were reproducible to ±0.1 ppm.

Infrared spectra were recorded at a scan speed of 39 cm^{-1} min^{-1} using a Perkin—Elmer model 337 grating spectrometer fitted with an external recorder. Spectra were calibrated with gaseous CO and reported bands are considered accurate to ±1 cm^{-1}. Cyclohexane was employed as solvent for all neutral complexes, and dichloromethane was used for $[CH_3CNRe(CO)_5][PF_6]$. Approximate force constants were calculated using the Cotton—Kraihanzel approximation [24]. In cases where infrared band positions not measured in this work were employed in force constant calculations, references are given in the footnotes to Table 2. In such cases force constants were recalculated from the published data to ensure internal consistency.

Acknowledgements

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