(2750 mL). A mixture of 3,3,3-trifluoropropyl bromide (264.7 g, 1.5 mol) and (3,3,3-trifluoropropyl)trichlorosilane (115.9 g, 0.5 mol) was added dropwise in 99 min, which kept the mixture gently refluxing with no external heat. The products were worked up as above, and GC analysis indicated the presence of $F_3CCH_2CH_2Si(OMe)_3$ (4%), $(F_3CCH_2CH_2)_2Si(OMe)_2$ (68%), and $(F_3CCH_2CH_2)_3SiOMe$ (28%). $n = 1.5\ \mathrm{mol}/(0.6 + 0.5)\ \mathrm{mol} = 1.36$.

Sodium (1.88 g, 0.082 mol) was dispersed in refluxing (3,3,3-trifluoropropyl)trimethoxysilane (16.54 g, 0.076 mol) and isooctane (25 mL). A mixture of 3,3,3-trifluoropropyl bromide (7.26 g, 0.041 mol) and trimethylchlorosilane (4.42 g, 0.041 mol) was added. GC analysis indicated the products were trimethylmethoxysilane (25%), $F_3CCH_2CH_2Si(OMe)_3$ (45.3%), $(F_3CCH_2CH_2)_2Si(OMe)_2$ (21%), and $(F_3CCH_2CH_2CH_2)_3SiOMe$ (5.5%). No $F_3CCH_2CH_2SiMe_3$ was detected. $n = 0.041\ \mathrm{mol}/0.076\ \mathrm{mol} = 0.7$. Me_3SiOMe did not enter into competitive reactions.

Sodium (152.8 g, 6.65 mol) was dispersed in refluxing (104 °C) methyltrimethoxysilane (2040 g, 15 mol). A mixture of allyl chloride (281.14 g, 3.67 mol, 10% excess) and methyltrichlorosilane (166 g, 1.11 mol) was added in 115 min, which was the maximum rate at which the condenser could condense the boil up. The products from several such runs were combined and distilled to recover allyl chloride and methyltrimethoxysilane followed by $CH_2{=}CHCH_2MeSi(OMe)_2$ (bp 128 °C; 366 g, 2.5 mol) and $(CH_2{=}CHCH_2)_2MeSiOMe$ (bp 153 °C; 66 g, 0.42 mol), leaving a small undistilled residue containing mostly what appeared to be $(CH_2{=}CHCH_2)_3MeSi$ and small amounts of several high-boiling unidentified compounds believed to be siloxanes. $n = 3.30\ \mathrm{mol}/(0.5 + 1.1)\ \mathrm{mol} = 0.21$.

Sodium (2.82 g, 0.12 mol) was dispersed in dimethyldi-*n*-hexoxysilane (34.3 g, 0.13 mol) at 104 °C, and a mixture of chlorobenzene (6.9 g, 0.06 mol) and dimethyldichlorosilane (4 g, 0.03 mol) was added. The temperature rose to 170 °C in 1 min. The mixture was cooled with an ice bath and kept at about 130 °C until the addition was completed in 7 min. Analysis by GC/MS indicated 100% yield of Me_2Ph SiO-*n*-Hex. $n = 0.06\ \mathrm{mol}/(0.13 + 0.03) = 0.38$.

Some of the products were needed at Dow Corning for miscellaneous applications, and these were scaled up and distilled to isolate alkoxysilanes that were more than 98% pure by GC analyses. Such examples include the allyl-, (trifluoropropyl)-, (ethoxymethyl)-, and phenylethoxysilanes. In each of these, yields by analytical distillation were in very good agreement with GC analysis.

Only 1 equiv of any chlorosilane should be mixed with the organic halide, and the organic groups on the chlorosilane should be the same as those on the alkoxysilane. If an excess of chlorosilane is used, the products contain chlorosilane impurities that are exceedingly difficult to separate. If the organic groups on the chlorosilane are not the same as those on the alkoxysilane, the products will be a mixture of organoalkoxysilanes with the different organo groups.

A convenient exception to this is the use of Me_3SiCl, which can be used in any case because it forms Me_3SiOR', which is volatile, easily separated from the other products, and slow to react with RNa to form Me_3SiR.

Data of Compounds Isolated Pure by Distillation. $EtOCH_2Si(OEt)_3$: bp 72 °C (10 mm); ^{1}H NMR δ 3.87 (6 H, q), 3.46 (2 H, q, 3.2 (2 H, s), 1.29 (12 H, t). $(EtOCH_2)_4Si$: bp 112 °C (10 mm); ^{1}H NMR δ 3.41 (8 H, s), 1.23 (12 H, t). $CH_2{=}CHCH_2MeSi(OMe)_2$: bp 128 °C (1 atm); ^{1}H NMR δ 5.75 (1 H, m), 3.5 (2 H, s), 1.64 (2 H, d), 0.13 (3 H, s). $(CH_2{=}CHCH_2)_2MeSiOMe$: bp 153 °C (1 atm); ^{1}H NMR δ 5.83 (2 H, d), 4.9 (4 H, m), 3.5 (3 H, s), 1.73 (4 H, d), 0.22 (3 H, s). $CH_2{=}CHCH_2Me_2SiOMe$: ^{1}H NMR δ 5.7 (1 H, m), 4.86 (2 H, m) 3.44 (3 H, s), 1.66 (2 H, d), 0.18 (6 H, s). $(F_3CCH_2CH_2)_3SiOMe$: bp 133 °C (71 mm); ^{1}H NMR δ 3.55 (3 H, s), 2.1 (6 H, m), 0.9 (4 H, m). $(F_3CCH_2CH_2)_2Si(OMe)$: bp 103 °C (76 mm); ^{1}H NMR δ 3.57 (6 H, s), 2.1 (4 H, m), 0.9 (4 H, m). $F_3CCH_2CH_2PhSi(OMe)_2$: bp 107 °C (12 mm); ^{1}H NMR δ 7.4 (5 H, m), 3.5 (6 H, s), 2.0 (2 H, m), 1.0 (2 H, m).

Acknowledgment. Initial experiments were carried out by Pamela Blatch.

Investigation of Substituent Effects in Substituted (η^5-Cyclopentadienyl)dicarbonylrhodium Compounds Using ^{103}Rh NMR and IR Data

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The effect of substituents on a series of ring-substituted (η^5-cyclopentadienyl)dicarbonylrhodium complexes was investigated by means of changes in C–O stretching frequencies as well as ^{103}Rh NMR chemical shifts. The effect of electron-donating and -withdrawing substituents on the ^{103}Rh NMR shift and CO stretching frequencies was found to be qualitatively consistent with the traditional model of dπ electron back-donation. The effect of the substituents was found to be neither a purely resonance or inductive phenomenon.

Introduction

^{103}Rh NMR spectroscopy has been used to gain information about the metal center in a variety of complexes.[1–6] The ^{103}Rh nucleus has a natural abundance of 100% and a nuclear spin of $^1/_2$. The combination of the resulting narrow resonance bands and very large chemical shift

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range provide a clear measurement of the rhodium environment.[1] For the compounds in the present study, the chemical shift range is over 200 ppm. While this is only a small fraction of the total chemical shift range of at least 10 000 ppm, from the shielded Rh(0) complexes to the deshielded Rh(III) complexes, it provides considerable discrimination of different environments. The greatest disadvantage of this technique is the low sensitivity of ^{103}Rh: only 0.2% that of ^{13}C. However, a greater relative abundance of ^{103}Rh gives a receptivity approximately 20% that of the ^{13}C nucleus, and much higher sensitivity can be achieved by the use of indirect (reverse) detection techniques.[6c] T_1 relaxation times are on the order of 5–50 s, and they are strongly field dependent.

No systematic investigation of the effect of substituents on the metal center in cyclopentadienyl metal compounds using transition-metal NMR spectroscopy has been undertaken. However, a study of ^{59}Co NMR spectroscopy as a probe into structure and catalytic activity has been reported by von Philipsborn and co-workers and demonstrated a correlation between catalytic activity of a series of pyridine synthesis catalysts and the ^{59}Co NMR shift of each catalyst.[7] The interaction between the substituent and the metal center is also demonstrated in this work. The ability to directly monitor the metal center by ^{103}Rh NMR provides an additional method to probe substituent effects.

A variety of substituent parameters have been devised to account for the effect of organic substituents on the reactivity of a given molecule. The Hammett parameters[8] σ_m and σ_p are derived from the rate of ionization of meta- and para-substituted benzoic acids, respectively. Taft[9-11] developed the substituent parameters $\sigma_R{}^\circ$ and σ_I that separate the resonance and inductive effects of a given substituent, respectively. The σ^n and $\sigma_p{}^\circ$ parameters developed by Yukawa et al.[12] measure the substituent effect on a reaction center insulated from an arene ring by a methylene group.

Other measurable physical parameters that have been used to study the effect of organic substituents in organometallic complexes include quarter-wave potentials,[13] ^{19}F NMR,[14] reaction kinetics,[15] and ionization energies obtained from photoelectron spectroscopy.[16] Some of the earliest work involving the use of IR spectroscopy as a tool for examining donor–acceptor properties was conducted by Tollman[17] using a series of substituted NiL_4 complexes with triply connected phosphorus ligands.

Experimental Section

Preparation of Substituted (η^5-Cyclopentadienyl)dicarbonylrhodium Compounds. Rhodium carbonyl chloride dimer, $[Rh(CO)_2Cl]_2$, was prepared by the method of McCleverty and Wilkinson.[18]

Preparations of the substituted $(\eta^5\text{-}C_5H_4R)Rh(CO)_2$ compounds were based on published procedures.[19-25] In general, 2 equiv of the appropriate substituted (η^5-cyclopentadienyl)metal salt was stirred under nitrogen with $[Rh(CO)_2Cl]_2$ in THF at room temperature for no less than 12 h. The resulting orange-red solution and metal chloride precipitate were filtered, and the filtrate was dried under high vacuum over 5% deactivated alumina. This was placed atop a 20-cm column of 5% deactivated alumina and eluted with hexane. In some instances, a small orange band of the unsubstituted compound $(\eta^5\text{-}C_5H_5)Rh(CO)_2$, resulting from impure substituted (η^5-cyclopentadienyl)metal salt, was obtained. With the exception of the nitro-substituted compound, all could be eluted with a mixture of 1:2 hexane–benzene. The nitro compound required benzene and was eluted as a bright-orange band. In all cases, the solvent was then removed under high vacuum. The syntheses for the methyl[19] and trimethylsilyl[23] derivatives are not clearly described in the literature, so separate experimental sections for these compounds are included.

Preparation of (η^5-Methylcyclopentadienyl)dicarbonylrhodium. Rhodium carbonyl chloride dimer (1.00 g, 2.57 mmol) was added to a 300-mL Schlenk flask containing 100 mL of THF under argon. To this solution was added an excess of (η^5-methylcyclopentadienyl)sodium (0.656 g, 6.43 mmol), prepared earlier by reaction of sodium hydride and freshly cracked methylcyclopentadiene in THF at 0 °C. The mixture was stirred at room temperature, and the color of the solution changed immediately to orange-brown. After 2 h, approximately 12 g of 5% deactivated alumina was added to the solution and the solvent removed under high vacuum. The dark-colored alumina was placed atop a 20-cm column of 5% deactivated alumina and eluted with hexane. (η^5-Methylcyclopentadienyl)dicarbonylrhodium eluted as a yellow band. Removal of the solvent afforded 0.32 g (26%) as a yellow-red oil. ^{1}H NMR ($CDCl_3$): δ 1.20 (s, CH_3), 5.2–5.5 (m, C_5H_4).

Preparation of [η^5-(Trimethylsilyl)cyclopentadienyl]dicarbonylrhodium. (Trimethylsilyl)cyclopentadiene (3.45 g, 25 mmol), prepared by the method of Abel and Dunster,[26] was added under argon to a round-bottom Schlenk flask containing 50 mL of hexane. To this solution was added 10 mL (25 mmol) of a 2.5 M solution of *n*-butyllithium in hexane. A white precipitate formed immediately. After 45 min of stirring, the solvent was removed under high vacuum to afford 3.25 g (86%) of $[\eta^5\text{-}C_5H_4(CH_3)_3Si]Li$ as a cream-colored solid.

The lithium salt (0.72 g, 5.0 mmol) was added to a 250-mL round-bottom Schlenk flask, containing 1.00 g (2.57 mmol) of rhodium carbonyl chloride dimer in 75 mL of diethyl ether. The diethyl ether solution had been previously cooled to −78 °C in a dry ice/acetone bath. After 60 s, the mixture turned a dark color. When the solution was warmed to room temperature, it was very dark brown. Approximately 8 g of 5% deactivated alumina was added to the solution and the solvent removed under high vacuum. The dark-colored alumina was placed atop a 15-cm column of 5% deactivated alumina and eluted with hexane.

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Table I. Values for Stretching Frequencies and Force Constants

substituent	stretching frequency (cm^{-1}) A	stretching frequency (cm^{-1}) E	force constant (mdyn/Å) K	force constant (mdyn/Å) Ki
$(CH_3)_3Si$	2045.4	1983.4	16.39	0.5043
H	2048.4	1985.3	16.43	0.5139
benzyl	2044.4	1981.8	16.37	0.5089
CH_3	2043.8	1980.7	16.36	0.5127
$COCH_3$	2057.4	1998.0	16.61	0.4864
Cl	2054.5	1993.5	16.55	0.4986
CHO	2060.7	2002.3	16.67	0.4791
NO_2	2067.8	2010.3	16.79	0.4735
phenyl	2046.7	1985.4	16.42	0.4991
$CO_2\,CH_3$	2057.2	1997.0	16.60	0.4928
vinyl	2042.5	1979.9	16.34	0.5084
CF_3	2061.7	2001.2	16.67	0.4963

Table II. Correlation of Substituent Parameters with IR Data

exptl[a] variable	substituent parameter (σ)	correln coeff	no. of compds
$\mu_{sym}(CO)$	$\sigma_p{}^\circ$	0.954	8
$\mu_{sym}(CO)$	$\sigma_R{}^\circ$	0.439	8
$\mu_{sym}(CO)$	σ_I	0.680	8
$\mu_{sym}(CO)$	σ^n	0.928	8
$\mu_{sym}(CO)$	σ_p	0.970	10
$\mu_{sym}(CO)$	σ_m	0.943	10
K	σ^n	0.935	8
K	σ_p	0.972	10
K	σ_m	0.945	10
K	σ_I	0.670	8
K	$\sigma_R{}^\circ$	0.450	8
K	$\sigma_p{}^\circ$	0.969	8

[a] Key: μ_{sym}, CO stretching frequency for symmetric motion (cm^{-1}); K, stretching force constant (mdyn/Å).

$[\eta^5$-(Trimethylsilyl)cyclopentadienyl]dicarbonylrhodium eluted as a yellow band. Removal of the solvent afforded 0.28 g (0.94 mmol, 19%) of the product. ^1H NMR: δ 0.20 (s, $SiMe_3$), 5.35–5.70 (m, C_5H_4).

Rhodium-103 NMR Shifts. The rhodium NMR spectra were collected at the University of Zürich with use of 10-mm sample tubes on a Bruker AM-400 NMR spectrometer equipped with a 20-mm low-frequency probe head. All measurements were made at 298 ± 1 K using a deuterium lock from the C_6D_6 solvent. The concentration of sample was approximately 50 mg/mL. The calculation of chemical shift has been described previously, and δ(Rh) values are relative to the arbitrary standard $\nu_{Rh}(\text{ref})/\nu_H(\text{TMS}) = 0.0316$.[5,6a]

Carbonyl Stretching Frequencies. All infrared spectra were collected at the University of Massachusetts on a Mattson Cygnus 100 FTIR spectrometer and a 0.1-mm path length solution cell, with sodium chloride windows. Spectra were recorded in hexane in order to minimize any solvent effects on the stretching frequencies. Resolution of 0.5 cm^{-1} was used in all cases. Solution concentration was adjusted so that the C–O stretching bands had a transmittance of no less than 10%.

Results and Discussion

Correlation of Infrared Data with Substituent Parameters. A variety of substituent parameters were plotted against stretching frequency data and estimated values for the bonding force constants for each member of the series. The force constants were calculated with use of the method of Cotton and Kraihanzel[27] and have been used by Bitterwolf[28] to probe the effect of various ring substituents in arene chromium carbonyl complexes. The values derived from this approach are given in Table I. Shown in Table II are the correlation coefficients and number of compounds used in each case.

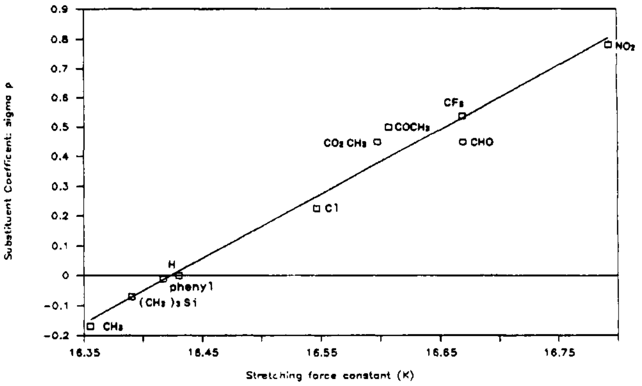

Figure 1. Correlation of CO stretching force constant with σ_p.

Table III. ^{103}Rh NMR Chemical Shift Data ($C_6\,D_6$) for Substituted $CpRh(CO)_2$ Compounds

substituent	^{103}Rh NMR shift (ppm)
$(CH_3)_3Si$	-1321.5
H	-1321.5
benzyl	-1278.2
CH_3	-1310.5
$COCH_3$	-1207.5
CHO	-1191.4
NO_2	-1116.6
CO_2CH_3	-1205.1

Table IV. Correlation of ^{103}Rh NMR Data with Substituent Parameters

substituent parameter (σ)	correln coeff	no. of compds
σ_n	0.933	5
$\sigma_p{}^\circ$	0.937	6
σ_p	0.941	6
$\sigma_R{}^\circ$	0.780	4
σ_I	0.91	5
σ_m	0.979	7

It is evident from Table II that the effect of the substituent on carbon monoxide stretching frequency is not a simple resonance or inductive effect. Correlation of all infrared data with $\sigma_R{}^\circ$ and σ_I is very poor. Neuse,[29] studying a series of substituted arene chromium tricarbonyl complexes, also found poor correlation with σ_I and σ_R. As with this work, Neuse found a reasonable correlation ($r = 0.96$) with σ_p, indicating the substituent appears to exert a mesomeric effect on the carbonyl group.

Bitterwolf[28] noted a significant correlation is obtained for the $\sigma_p{}^\circ$ parameter with both the symmetric stretching frequency and the force constant (K). This parameter measures the substituent effect on a reaction center insulated from an arene ring by a methylene group. The data in Table II also show correlation with $\sigma_P{}^\circ$.

Correlation of force constants with the Hammett substituent parameters, σ_m and σ_p, are better than those obtained when $\sigma_R{}^\circ$ and σ_I are used. Shown in Figure 1 is the plot of σ_p versus the stretching force constant (K). Basolo,[15] using only six compounds, also found good correlation of σ_p with the carbonyl stretching frequency but not with reaction kinetics. This observation was attributed to differences in reaction mechanism.

Unlike the arene chromium carbonyl compounds studied by Bitterwolf,[28] the aldehyde derivative in the present study showed no unusual behavior. In fact, examination of the data shows no one compound consistently deviates from the general pattern of behavior.

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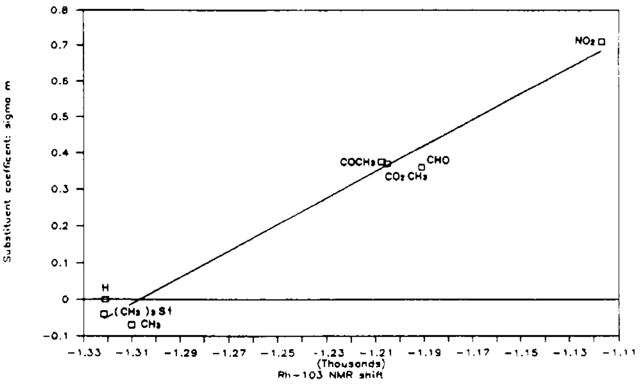

Figure 2. Correlation of rhodium-103 NMR data with σ_m.

^{103}Rh NMR Data. Table III gives the ^{103}Rh NMR chemical shift data for a series of substituted CpRh(CO)$_2$ compounds. The expected qualitative effects of an electron-withdrawing or -donating substituent on the chemical shift of the rhodium nucleus are seen. For instance, a highy electron-withdrawing group such as the nitro group (−1116.6 ppm) results in a ^{103}Rh chemical shift ca. 200 ppm downfield from the parent compound (−1321.5 ppm).

The data obtained from ^{103}Rh NMR provided significant ($R^2 > 0.91$) correlations with five substituent parameters. With the notable exception of the inductive Taft parameter, σ_I, the correlation coefficients obtained from the C–O stretching frequencies were comparable for any given parameter.

The regression data for correlation of ^{103}Rh NMR shift with the substituent parameters are summarized in Table IV.

As with the IR data, correlation coefficients in excess of 0.9 for the NMR data were obtained with σ_p, $\sigma_p{}^o$, σ_m (Figure 2), and σ^n. Unlike the IR data, however, a significant correlation of σ_I, the inductive Taft parameter, with NMR data was seen. This could be rationalized in terms of the NMR data being less influenced by steric interactions and therefore a more direct measure of the electron-withdrawing or -donating abilities of the ring substituent.

Plots of the ^{103}Rh NMR shift data for eight compounds against both the symmetric (Figure 3) and asymmetric stretching bands yielded correlation coefficients of approximately 0.92 in both cases. The qualitative trend is that expected from the traditional model of metal dπ electron density back-donation to the coordinated carbon monoxide. The effect of adding an electron-withdrawing group such as NO$_2$ or CHO to the ring is to shift the ^{103}Rh NMR resonance downfield, relative to the parent compound, and to increase the symmetric and asymmetric C–O stretching frequencies. The latter effect is caused by reduced electron density available for back-donation to the coordinated carbon monoxide antibonding orbitals. Steric effects of a bulky substituent would not be taken into account in such a simple model. In addition, the difference in solvents between the two studies may account for deviation from a simple linear relationship between the NMR and IR data. While little solvent–solute interaction is expected for the hexane used in the IR studies, some interaction would be expected for the aromatic and more polar benzene used to collect the NMR data.

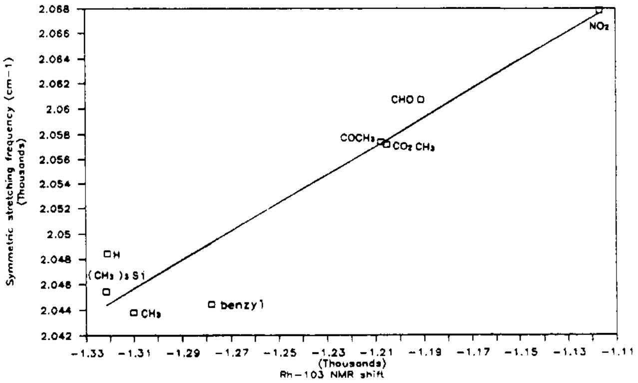

Figure 3. Symmetric stretching frequency vs rhodium-103 chemical shift.

Conclusion

^{103}Rh NMR and CO stretching frequency data provide a means to monitor the effect of ring substituents in monosubstituted (η^5-cyclopentadienyl)dicarbonylrhodium compounds. The effect of substituents on the cyclopentadienyl ring is neither a simple resonance or inductive effect, as neither data correlates well with Taft parameters. The effect of ring substituents on the CO stretching frequencies is in agreement with the model of metal dπ electron back-donation.

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