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Note Added in Proof. At the suggestion of a reviewer the generality of the reaction was tested by carrying out

the reaction of *o*-FFp with phenyllithium. The dark brown/black product obtained was characterized by mass spectroscopy and ^1H NMR as an analogue of **2** with the phenyl group replacing the *o*-fluorobiphenyl moiety. The yield was >90%.

Supplementary Material Available: A table of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

Notes

Mixed Rhenium and Chromium Carbonyl Complexes of Aroylcyclopentadienyl Ligands

Niall J. Gogan* and Sheila I. De Silva

Department of Chemistry, Memorial University of Newfoundland,
St. John's, Newfoundland, Canada A1B 3X7

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Summary: A series of (aroylcyclopentadienyl)rhenium tricarbonyls $(\eta^5\text{-RC}_6\text{H}_4\text{COC}_5\text{H}_4)\text{Re}(\text{CO})_3$, R = H, *o*-CH₃, *p*-CH₃, *p*-OCH₃, *o*-F, *p*-Cl and their $\text{Cr}(\text{CO})_3$ (η^6 -arene) $\text{Cr}(\text{CO})_3$ complexes have been prepared and characterized and studied by IR and ^1H NMR spectroscopy. The carbonyl stretching frequencies of the $\text{Re}(\text{CO})_3$ group and the cyclopentadienyl proton resonances indicate π -electron withdrawal through the ligand system by the $\text{Cr}(\text{CO})_3$ group.

Complexes with two or more π -donor sites have been of interest in our laboratory for a number of years. A major reason for studying such complexes has been to determine the extent of electron delocalization through an extended π -system and particularly to study the effect of metal complexation on electron delocalization. All of the complexes reported so far by us have involved only first-row transition metals.

There are many examples in the literature of organometallic complexes with two metal atoms, at least one of which is a second- or third-row element. Almost all of these have the two metal atoms directly bonded, such as $\text{Cp}_2\text{Re}(\text{H})\text{Mn}(\text{CO})_4$,¹ or joined by simple bridging groups such as hydrido and alkenyl.² Pyrazine had also been used as a bridging ligand.³ Another interesting example of a bridging ligand is in $\text{CpCoC}_8\text{H}_8\text{Mo}(\text{CO})_3$, which has two forms, one of which has the metals joined by the cyclooctatetraene ring without a metal-metal bond.⁴ None of these compounds have extended bridging ligands, particularly extended π -systems, and hence do not lend themselves to the study of through-ligand metal-metal interaction.

Table I. Elemental Analyses, Melting Points, and Percent Yields of $\text{RC}_6\text{H}_4\text{COC}_5\text{H}_4\text{Re}(\text{CO})_3$

R	yield, %	mp, °C	C		H	
			found	calcd	found	calcd
H	23.0	97-98	41.16	40.93	2.24	2.06
<i>o</i> -CH ₃	37.1	114-115	42.23	42.31	2.47	2.44
<i>p</i> -CH ₃	52.7	89-90	42.77	42.31	2.57	2.44
<i>p</i> -OCH ₃	23.2	134-135	40.99	40.87	2.52	2.36
<i>o</i> -F	40.0	100-101	39.27	39.32	1.90	1.76
<i>p</i> -Cl	34.0	107-108	39.24	37.96	2.31	1.70

Fulvalene lends itself to the formation of dimetalla complexes, most of which have the metals directly bonded. There are some examples without metal-metal bonding, and some of these involve heavier metals.⁵

Recently Helvenston and Lynch⁶ reported three triindenyl complexes in which two or three $\text{Re}(\text{CO})_3$ groups are η^5 -bonded to the five-membered rings. These molecules do lend themselves to the study of through-ligand metal-metal interaction (or intramolecular metal-metal cooperativity). The report, however, was of only one ligand and involved only one metal, so no comparisons were possible across a series of ligands or between metals.

The most extensive series of complexes with two or more π -donor sites reported so far have been (η^5 -aroylcyclopentadienyl)manganese tricarbonyls⁷ and their $\text{Cr}(\text{CO})_3$ complexes.⁸ In this paper the preparation and IR and ^1H NMR spectra of similar $\text{Re}(\text{CO})_3$ complexes are reported and discussed and the results are compared with those of the corresponding manganese complexes.

Results and Discussion

(Aroylcyclopentadienyl)rhenium tricarbonyls are white crystalline materials with melting points in the range of 97-135 °C (Table I). The C and H analyses are in good

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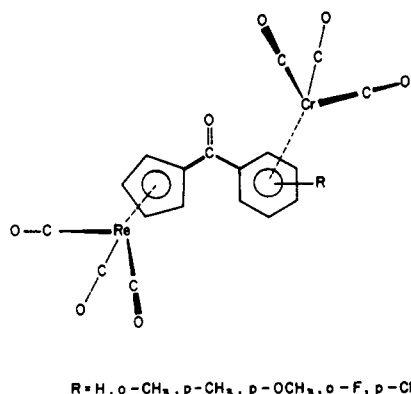


Figure 1.

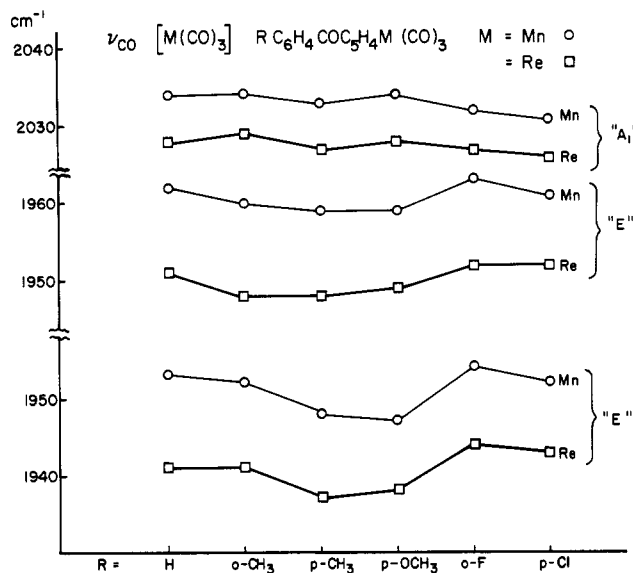


Figure 2.

agreement with the calculated values (Table I). All show the following bands in the ν_{CO} region of the IR spectra: a relatively sharp band around 2028 cm^{-1} , a split band in the 1937–1952- cm^{-1} range, and a band in the 1649–1670- cm^{-1} region. The first two bands are typical of a $\text{M}(\text{CO})_3$ group with the highest energy absorption corresponding to the A_1 band in ideal C_{3v} symmetry and the split band to the E vibration, the splitting being typical for these highly unsymmetrical ligands.^{7,8} The lowest energy band is readily assigned to the ketone ν_{CO} . The mass spectra of all the compounds show the molecular ion and those corresponding to the loss of two and three CO groups. The ^1H NMR spectra show resonances in the usual range for complexed Cp rings (δ 5.4–6.0) and for uncomplexed benzene rings (δ 6.9–7.9).

The corresponding $\text{Cr}(\text{CO})_3$ complexes (Figure 1) show an extra pair of bands in the ν_{CO} region at around 1986 cm^{-1} (A_1) and in the 1910–1950- cm^{-1} (split E) range. The ^1H NMR spectra show the Cp resonances only slightly shifted from the values in the parent compounds and the benzene ring resonances shifted upfield by 1.5–2.2 ppm. The mass spectra show ions corresponding to the sequential loss of two, three, four, five, and six CO's. These results demonstrate that the compounds are (η^6 -arene) $\text{Cr}(\text{CO})_3$ complexes. These are yellow or orange crystalline materials with melting points as follows ($^\circ\text{C}$): H, 125–127; o-CH₃, 161–162; p-CH₃, 106–108; p-OCH₃, 163–164; o-F, 124–126.

The IR and ^1H NMR data are shown graphically in a series of figures with the values for the corresponding Mn compounds^{7,8} given for comparison. In each figure the

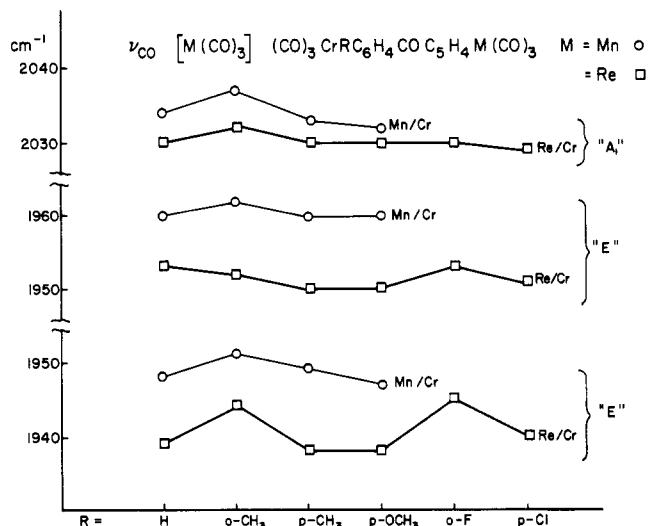


Figure 3.

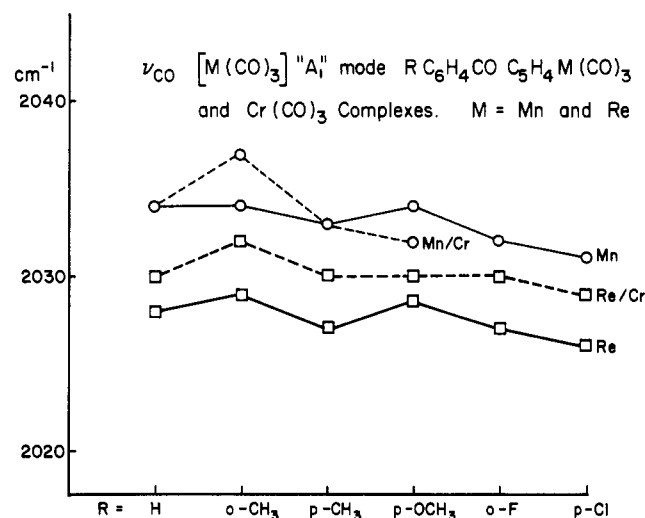


Figure 4.

substituents on the benzene ring are shown equally spaced along the abscissa.

Carbonyl stretching frequencies (ν_{CO}) of the $\text{M}(\text{CO})_3$ group (M = Mn, Re) for the parent compounds, i.e. those without the $\text{Cr}(\text{CO})_3$ group, are shown in Figure 2. Substituents on the benzene ring have very little effect on the stretching frequencies of either the Re or Mn series. There is, however, a substantial difference between the Re and Mn compounds, with the values for the Re compounds consistently lower in energy than for the Mn compounds. The " A_1 " mode is sharper than the "E" bands, and therefore, more reliance is placed on it when the results are interpreted in terms of electron distribution. Figure 3 gives the results for the corresponding $\text{Cr}(\text{CO})_3$ complexes, with the values for the Re series again being at lower wavenumber than for the Mn compounds. The full series of $\text{Cr}(\text{CO})_3$ complexes did not form in the manganese case.⁸

The effect of $\text{Cr}(\text{CO})_3$ complexation is demonstrated in Figure 4 by plotting the " A_1 " mode results for all four series. There is no consistent trend for the Mn compounds, but the values for $\text{Re}(\text{CO})_3$ are higher in all cases for the $\text{Cr}(\text{CO})_3$ complexes as compared to those for the parent compounds. Thus, there is clear evidence that the $\text{Cr}(\text{CO})_3$ group is having a consistent effect on the CO's of the $\text{Re}(\text{CO})_3$ group, indicating electron delocalization through the ligand system. The higher values for the $\text{Cr}(\text{CO})_3$

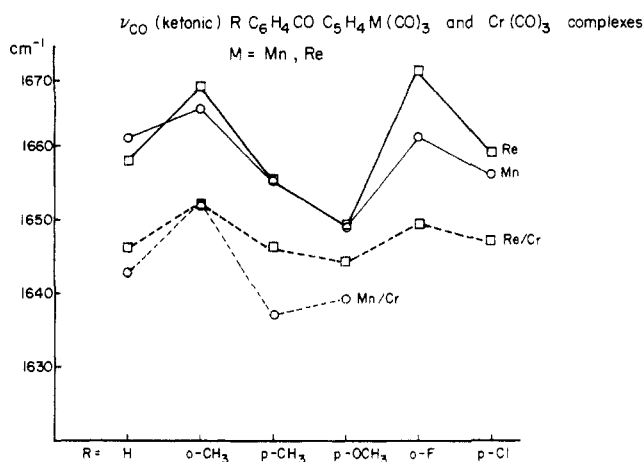


Figure 5.

complexes denote a higher bond order for the CO's of $\text{Re}(\text{CO})_3$, indicating π -electron withdrawal from the CO antibonding orbitals.

In the case of the $\text{Cr}(\text{CO})_3$ ν_{CO} values, the differences between the Mn and Re series are small and, therefore, we draw no conclusions regarding electron delocalization from them.

The ν_{CO} (ketonic) values for all four series are given in Figure 5. There is a strong substituent effect as well as a very substantial effect by the $\text{Cr}(\text{CO})_3$ group for both the Mn and Re compounds. There is, however, no consistent difference between the values for the Mn and the corresponding Re compounds, and in several cases the same value is observed. This is strong evidence to support the conclusion that the ketonic CO is much more associated with the benzene ring than with the Cp ring.

The ^1H NMR resonances of the Cp protons are given in Figure 6. The most striking feature is that the resonances for all the Re compounds are at much lower fields than for the Mn compounds, supporting the conclusion from the IR data that Re is more electron withdrawing than Mn. The $\text{Cr}(\text{CO})_3$ complexes have resonances at considerably lower fields than the parent compounds for the α -protons and in almost all cases for the β -protons. This demonstrates that the electron-withdrawing effect of the $\text{Cr}(\text{CO})_3$ group is transmitted through the ligand system to the Cp protons.

Nesmeyanov et al.⁹ studied the carbonyl bands in the IR spectra of a series of substituted $\text{CpRe}(\text{CO})_3$ compounds and their Mn analogues. They found that the transmission of substituent effects was inductive in nature and was more effective in the Mn compounds than in the corresponding Re analogues. In the cases described in this paper, where the effects are transmitted through an extended π -system, it is found that the transmission is more effective in the Re compounds. It would thus appear that π -electron transmission is more effective in the Re compounds, whereas σ -effects are more easily transmitted in the Mn analogues.

Experimental Section

Melting points were obtained with use of a Fisher-Johns block apparatus and are reported uncorrected. The C and H analyses were performed by Canadian Microanalytical Service, Vancouver, BC, Canada. The IR spectra were recorded in CCl_4 solution on a Perkin-Elmer 283 spectrometer, and the ν_{CO} values are reproducible to within 1 cm^{-1} . A Bruker WP 80 spectrometer was used to obtain ^1H NMR spectra in CDCl_3 solution with tetramethyl-

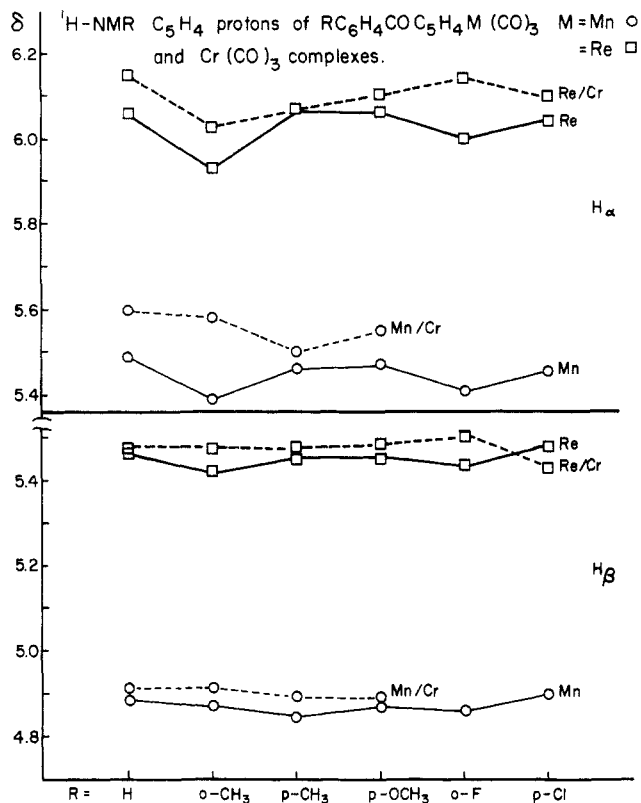


Figure 6.

silane as internal reference, and the results are expressed in ppm (δ values; precision 0.01 ppm). Mass spectra were recorded on a VG Micromass 7070 HS spectrometer.

Preparations. All the preparations were carried out under an atmosphere of nitrogen (UHP grade).

Cyclopentadienylrhenium tricarbonyl ($\eta^5\text{-Cp}$) $\text{Re}(\text{CO})_3$ was prepared in several batches by using the method of Green and Wilkinson.¹⁰ Rhenium carbonyl (0.5 g) was refluxed in an excess of dicyclopentadiene for 6 h. The crude product was purified by flash chromatography on silica gel with ethyl acetate/petroleum ether (60–80 °C) (1:1) to yield 0.4 g (80%) of white crystals, mp 114–115 °C.

(Aroylcyclopentadienyl)rhenium tricarbonyls were prepared according to the method of Fischer and Fellman¹¹ by Friedel-Crafts arylation of ($\eta^5\text{-Cp}$) $\text{Re}(\text{CO})_3$ with the corresponding aryl chloride in methylene chloride. In the case of the parent compound, $\text{CpRe}(\text{CO})_3$ (0.409 g) yielded 0.564 g (23%). Yields (%) are given in Table I.

The $\text{Cr}(\text{CO})_3$ complexes were prepared by the same method used for the corresponding manganese compounds.⁸ The yields varied from 6% for the $p\text{-OCH}_3$ derivative to 60% for the $p\text{-CH}_3$ complex.

Acknowledgment. We thank Memorial University of Newfoundland for financial support.

Registry No. ($\eta^5\text{-Cp}$) $\text{Re}(\text{CO})_3$, 12079-73-1; $\text{C}_6\text{H}_5\text{COC}_5\text{H}_4\text{Re}(\text{CO})_3$, 12267-07-1; $o\text{-CH}_3\text{C}_6\text{H}_4\text{COC}_5\text{H}_4\text{Re}(\text{CO})_3$, 126823-46-9; $p\text{-CH}_3\text{C}_6\text{H}_4\text{COC}_5\text{H}_4\text{Re}(\text{CO})_3$, 126823-47-0; $p\text{-OCH}_3\text{C}_6\text{H}_4\text{COC}_5\text{H}_4\text{Re}(\text{CO})_3$, 126823-48-1; $o\text{-FC}_6\text{H}_4\text{COC}_5\text{H}_4\text{Re}(\text{CO})_3$, 126847-93-6; $p\text{-ClC}_6\text{H}_4\text{COC}_5\text{H}_4\text{Re}(\text{CO})_3$, 126823-49-2; ($\text{CO})_3\text{CrC}_6\text{H}_5\text{COC}_5\text{H}_4\text{Re}(\text{CO})_3$, 126823-50-5; ($\text{CO})_3\text{Cr}(o\text{-CH}_3\text{C}_6\text{H}_4)\text{COC}_5\text{H}_4\text{Re}(\text{CO})_3$, 126823-51-6; ($\text{CO})_3\text{Cr}(p\text{-CH}_3\text{C}_6\text{H}_4)\text{COC}_5\text{H}_4\text{Re}(\text{CO})_3$, 126823-52-7; ($\text{CO})_3\text{Cr}(p\text{-OCH}_3\text{C}_6\text{H}_4)\text{COC}_5\text{H}_4\text{Re}(\text{CO})_3$, 126847-94-7; ($\text{CO})_3\text{Cr}(o\text{-FC}_6\text{H}_4)\text{COC}_5\text{H}_4\text{Re}(\text{CO})_3$, 126823-53-8; ($\text{CO})_3\text{Cr}(p\text{-ClC}_6\text{H}_4)\text{COC}_5\text{H}_4\text{Re}(\text{CO})_3$, 126847-95-8; $\text{C}_6\text{H}_5\text{COCl}$, 98-88-4; $o\text{-CH}_3\text{C}_6\text{H}_4\text{COCl}$, 933-88-0; $p\text{-CH}_3\text{C}_6\text{H}_4\text{COCl}$, 874-60-2; $p\text{-OMeC}_6\text{H}_4\text{COCl}$, 100-07-2; $o\text{-FC}_6\text{H}_4\text{COCl}$, 393-52-2; $p\text{-ClC}_6\text{H}_4\text{COCl}$, 122-01-0; rhenium carbonyl, 14285-68-8; dicyclopentadiene, 77-73-6.

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