Stereochemical Non-rigidity of the Indenyl Ligand in the Compound [CrRh(μ-CO)$_2$(CO)$_2$(η-C$_9$H$_7$)(η-C$_6$H$_3$Me$_3$-1,3,5)] *

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Examination of the variable temperature ^{13}C-{^{1}H} data for the compound [CrRh(μ-CO)$_2$(CO)$_2$-(η-C$_9$H$_7$)(η-C$_6$H$_3$Me$_3$-1,3,5)] reveals dynamic behaviour involving hindered rotation of the η-C$_9$H$_7$ ligand; with $\Delta G^{\ddagger}$ at -32 °C, 45.2 ± 1 kJ mol^{-1}.

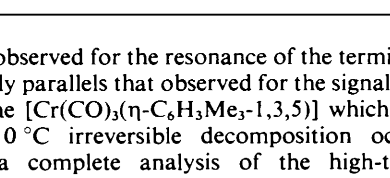
We recently prepared the chromium–rhodium complex [CrRh(μ-CO)$_2$(CO)$_2$(η-C$_9$H$_7$)(η-C$_6$H$_3$Me$_3$-1,3,5)] (1), and observed that its ^{13}C-{^{1}H} n.m.r. spectrum varied with temperature.[1] When measured at -70 °C the Cr(μ-CO)$_2$Rh system gives rise to two resonances, each occurring as a doublet, due to the ^{103}Rh–^{13}C coupling. On warming, however, the signals collapse, suggesting the onset of dynamic behaviour. Herein we describe a more detailed ^{13}C-{^{1}H} n.m.r. study, carried out in order to elucidate the mechanism of the process. We had previously considered two possibilities: either rotation of the Rh(CO)(η-C$_9$H$_7$) group about the Cr–Rh axis, or rotation of the η-C$_9$H$_7$ ligand about an axis through the rhodium and the centroid of the five-membered ring of the indenyl group.

Results and Discussion

Complex (1), highly enriched in ^{13}CO, was prepared [1] by co-photolysis of [Cr(CO)$_3$(η-C$_6$H$_3$Me$_3$-1,3,5)] and [Rh(^{13}CO)$_2$-(η-C$_9$H$_7$)] in tetrahydrofuran at 0 °C. Extensive scrambling of carbonyl groups occurs so that all carbonyl sites in (1) become labelled. The product is generally contaminated with [Cr(CO)$_3$-(η-C$_6$H$_3$Me$_3$-1,3,5)], the presence of which is revealed spectroscopically (i.r. and n.m.r.). Earlier we reported [1] an *X*-ray crystallographic study on [CrRh(μ-CO)$_2$(CO)$_2$(η-C$_5$Me$_5$)-(η-C$_6$H$_6$)], a compound closely related to (1), differing by the presence of an η-C$_5$Me$_5$ rather than a η-C$_9$H$_7$ ligand. The *X*-ray results showed that in [CrRh(μ-CO)$_2$(CO)$_2$(η-C$_5$Me$_5$)-(η-C$_6$H$_6$)] the η-C$_6$H$_6$ and η-C$_5$Me$_5$ ligands are *trans* with respect to the metal–metal bond, and that the molecule has a crystallographically imposed mirror plane bisecting the C$_6$H$_6$ and C$_5$Me$_5$ rings and incorporating the two terminal CO groups. Thus the two bridging CO ligands are symmetry related. Although an *X*-ray diffraction study has not been carried out on (1), there is no reason to believe that its structure is fundamentally different from that of [CrRh(μ-CO)$_2$(CO)$_2$(η-C$_5$Me$_5$)(η-C$_6$H$_6$)]. Hence it was surprising to observe [1] two signals for the μ-CO groups in the ^{13}C-{^{1}H} n.m.r. spectrum at low temperatures.

The results of the new study using the ^{13}CO-enriched complex (1) are shown in the accompanying Figure. The two resonances for the μ-CO ligands seen clearly as doublets [*J*(RhC) *ca.* 20 Hz] at -75 °C coalesce at *ca.* -30 °C, and a single and reasonably sharp resonance appears at 20 °C. There are no substantial changes in the signals due to the terminal CO ligands as a function of temperature, apart from some slight broadening of the bands as the temperature is raised. The broadening observed for the resonance of the terminal Cr–CO group roughly parallels that observed for the signals of the CO ligands in the [Cr(CO)$_3$(η-C$_6$H$_3$Me$_3$-1,3,5)] which is present. Above *ca.* 0 °C irreversible decomposition occurs, thus precluding a complete analysis of the high-temperature limiting spectrum. Hence it was not possible to observe coupling of the μ-^{13}CO ligands with ^{103}Rh at temperatures above coalescence. Nevertheless, it is evident that the dynamic process does not involve the two terminal CO ligands, and hence bridge–terminal site exchange does not occur. Moreover, a *cis–trans* isomerisation process is unlikely since only one resonance is observed for each terminal CO group at -75 °C, and the two μ-CO peaks are of equal intensity. The latter feature would be highly unlikely if these intensities reflected populations of *cis* and *trans* isomers, respectively.

The low-temperature spectrum indicates the absence of a mirror plane in (1), while the high-temperature spectrum suggests the presence of a pseudo mirror plane. Thus the results are interpretable on the basis of hindered rotation of the indenyl ring system about an axis through the rhodium, *i.e.* the η-C$_9$H$_7$ group prefers a conformation which destroys the potential mirror plane (see below).



For the apparent two-site CO exchange process the rate *k* is given by equation (i), where $|\nu_A - \nu_B|$ is the separation (in

$$k = \frac{\pi|\nu_A - \nu_B|}{\sqrt{2}} \qquad \text{(i)}$$

Hz) of the two signals in the absence of exchange.[2] For (1), $|\nu_A - \nu_B| = 335$ Hz at 198 K from which $\Delta G_{T_c}^{\ddagger} = 45.2 \pm 1$ kJ mol^{-1}. It is interesting to compare the magnitude of this energy barrier to rotation with the results for other systems.

In metal π-complexes containing cyclic η^n-C$_n$ ($n = 3$—8) ligands, the barrier to internal rotation about the *n*-fold axis is generally so low that it cannot be measured by n.m.r. techniques.[3,4] However, the activation energy for ring rotation can be increased by disubstitution with bulky groups, as in the compounds [U(η-C$_8$H$_6$Bu$^t_2$-1,4)$_2$], [Fe(η-C$_5$H$_3$Bu$^t_2$-1,3)$_2$],[5] and [Ru(SiCl$_3$)$_2$(CO)(η-C$_6$H$_4$Bu$^t_2$-1,4)][6] for which $\Delta G_{T_c}^{\ddagger} = 34.7$, 54.8, and 51 kJ mol^{-1}, respectively. In the species [CoH(PMe$_3$)$_2$(η-C$_5$H$_3$RR$'$-1,3)]$^+$ and [Co(PMe$_3$)$_2$-

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* Di-μ-carbonyl-1,2-dicarbonyl-1-η-indenyl-2-(1$'$—6$'$-η-1$'$,3$'$,5$'$-trimethylbenzene)rhodiumchomium(*Rh*^{1}—*Cr*^{2}).

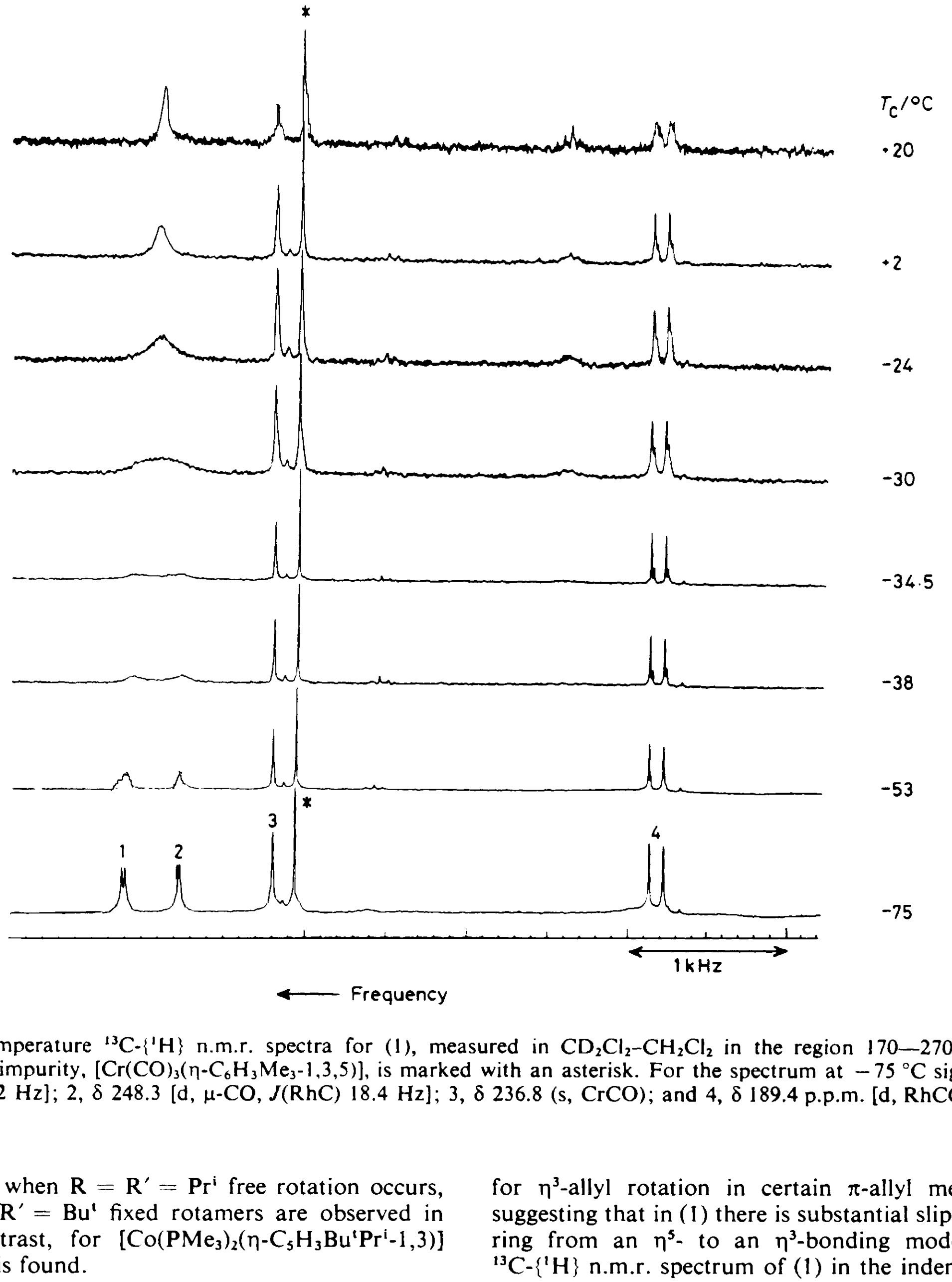

Figure. Variable temperature ^{13}C-{^{1}H} n.m.r. spectra for (1), measured in CD_2Cl_2-CH_2Cl_2 in the region 170—270 p.p.m. The peak (δ 234.0) due to the impurity, [Cr(CO)$_3$(η-$C_6H_3Me_3$-1,3,5)], is marked with an asterisk. For the spectrum at −75 °C signals are 1, δ 255.0 [d, μ-CO, *J*(RhC) 22 Hz]; 2, δ 248.3 [d, μ-CO, *J*(RhC) 18.4 Hz]; 3, δ 236.8 (s, CrCO); and 4, δ 189.4 p.p.m. [d, RhCO, *J*(RhC) 88 Hz]

(η-C_5H_3RR′-1,3)], when R = R′ = Pr^i free rotation occurs, whereas for R = R′ = Bu^t fixed rotamers are observed in solution.[7] In contrast, for [Co(PMe$_3$)$_2$(η-C_5H_3Bu^{t}Pr^i-1,3)] hindered rotation is found.

In the above compounds the barrier to rotation is predominantly due to steric interactions between ring substituents and the metal-ligand fragments with which they are associated. However, molecular orbital calculations [4,8] suggest that 1,3- or 1,3,4-substitution on an η-C_5H_5 ring, or replacement of carbons by atoms of another element, will result in the largest rotational barriers on the basis of electronic factors rather than simply steric effects. The heteroatom effect has been conclusively demonstrated [3] for a series of isomeric metallacarbaborane complexes containing η-$C_2B_9H_{10}$R (R = H, Me, Bu^n, or Ph) ligands with planar five-membered bonding faces.

Although stereochemical non-rigidity of the haptotropic type [9] has been observed in certain indenyl metal complexes, we are not aware of any previous determinations of the barrier to hindered rotation of this ligand as observed for (1). Taking into account the low barriers for η^5-C_5 ring rotations in sterically undemanding systems,[2] discussed above, the value of *ca.* 45 kJ mol^{-1} for indenyl rotation in (1) appears surprisingly large. This value, however, is in the range observed [2,10] for η^3-allyl rotation in certain π-allyl metal compounds, suggesting that in (1) there is substantial slippage of the C_9H_7 ring from an η^5- to an η^3-bonding mode. Although the ^{13}C-{^{1}H} n.m.r. spectrum of (1) in the indenyl region is very complicated, at low temperatures the appearance of a doublet signal at δ 104.93 p.p.m. [*J*(RhH) 5 Hz] for the unique (C^2) carbon of the five-membered ring shows that it is this ring rather than the six-membered ring which is co-ordinated to the metal.[11] Slip-fold distortions [12] in certain indenyl metal complexes have been invoked [13] to account for their enhanced reactivity compared with their cyclopentadienyl analogues, and there is convincing *X*-ray crystallographic evidence [14] for slippage of one of the indenyl ligands in [W(CO)$_2$(η-C_9H_7)$_2$], thereby avoiding a formal 20-electron count at the tungsten.

Interestingly, the structural studies [1] on [CrRh(μ-CO)$_2$-(CO)$_2$(η-C_5Me_5)(η-C_6H_6)] revealed distinct differences in the Rh–C(C_5Me_5) distances suggesting stronger bonding to three of the carbons compared with that to the other two. The analogous complex [MnRh(μ-CO)$_2$(CO)$_2$(η-C_5H_5)(η-C_5Me_5)] also contains an η-C_5Me_5 ring with slippage along an axis coincident with the crystallographic mirror plane.[15] The potential energy surface for slippage of an ML$_3$ fragment [*e.g.* Fe(η-C_5H_5)$^+$] with respect to an η^5-indenyl ligand has recently been described.[9] The ground-state minimum occurs for the iron slipped away from the central carbon–carbon (C^{3a}–C^{7a}) bond. Movement of the metal in this direction requires significantly less energy than movement towards the central bond.

The above results lead us to propose that (1) has a ground-state geometry in which the η-C_9H_7 ring system is significantly slip-folded towards η^3-bonding away from the C_6 ring, and that the orientation of the ligand is such that the slippage is perpendicular to the mirror plane of the $CrRh(\mu\text{-}CO)_2(CO)_2$-(η-$C_6H_3Me_3$-1,3,5) fragment. It is the latter property which makes observation of the dynamic process possible on the n.m.r. time-scale.

Experimental

The ^{13}C-{^1H} n.m.r. spectra were measured on a JEOL FX 200 spectrometer. The synthesis of (1)[1] was carried out under argon using Schlenk-tube techniques, and freshly distilled oxygen-free solvents. A 450-W medium-pressure mercury vapour lamp was used in the synthesis. The ^{13}CO enrichment was carried out by degassing (high vacuum line) a pentane (10 cm^3) solution of [$Rh(CO)_2$(η-C_9H_7)] (0.07 g, 0.25 mmol) followed by admission of the ^{13}CO (11.3 cm^3, 0.5 mmol) to the flask. The mixture was allowed to equilibrate for *ca.* 3 h before the mononuclear rhodium compound was used in the preparation of (1).

References

1 R. D. Barr, M. Green, K. Marsden, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1983, 507.
2 B. E. Mann, in ' Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, Oxford, 1982, vol. 3, ch. 20.
3 T. B. Marder, R. T. Baker, J. A. Long, J. A. Doi, and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1981, **103**, 2988 and refs. therein.
4 T. A. Albright, P. Hofmann, and R. Hoffmann, *J. Am. Chem. Soc.*, 1977, **99**, 7546.
5 W. D. Luke and A. Streitwieser, *J. Am. Chem. Soc.*, 1981, **103**, 3241.
6 R. K. Pomeroy and D. J. Harrison, *J. Chem. Soc., Chem. Commun.*, 1980, 661.
7 W. Hofmann, W. Buchner, and H. Werner, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 795.
8 T. A. Albright and R. Hoffmann, *Chem. Ber.*, 1978, **111**, 1578; T. A. Albright, R. Hoffmann, Y. Tse, and T. D. Ottavio, *J. Am. Chem. Soc.*, 1979, **101**, 3812.
9 T. A. Albright, P. Hofmann, R. Hoffmann, C. P. Lillya, and P. A. Dobosh, *J. Am. Chem. Soc.*, 1983, **105**, 3396 and refs. therein.
10 J. W. Faller, *Adv. Organomet. Chem.*, 1977, **16**, 211.
11 F. H. Köhler, *Chem. Ber.*, 1974, **107**, 570.
12 D. M. P. Mingos, in ' Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, Oxford, 1982, vol. 3, ch. 19.
13 P. Caddy, M. Green, E. O'Brien, L. E. Smart, and P. Woodward, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 648; *J. Chem. Soc., Dalton Trans.*, 1980, 962.
14 A. N. Nesmeyanov, N. A. Ustynyuk, L. G. Makarova, V. G. Andrianov, Yu.T. Struchkov, S. Andrae, Yu.A. Ustynyuk, and S. G. Malyugina, *J. Organomet. Chem.*, 1978, **159**, 189.
15 M. L. Aldridge, M. Green, J. A. K. Howard, G. N. Pain, S. J. Porter, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1982, 1333.

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