Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

CHEMISTRY OF METHYLIDYNETRICOBALT ENNEACARBONYLS VII*. PREPARATION AND PROPERTIES OF A FLUXIONAL MOLECULE, $PhCCo_3(CO)_6C_8H_8$

B. H. ROBINSON AND J. SPENCER
Chemistry Department, University of Otago, Dunedin (New Zealand)

(Received May 18th, 1971)

SUMMARY

The preparation and spectral properties of $PhCCo_3(CO)_6C_8H_8$ are described. This labile complex has the ligand bound to three cobalt atoms beneath the basal Co_3 triangle. Its fluxional behaviour has been investigated and the predominant rearrangement pathway shown to be a sequence of 1,2 shifts. Other methylidynetricobalt enneacarbonyls do not form similar derivatives.

INTRODUCTION

Recently we described[1] a number of labile arene derivatives, $YCCo_3(CO)_6$-(arene), in which the arene was symmetrically coordinated to one cobalt atom of the Co_3C cluster. This work and the X-ray analysis of $PhCCo_3(CO)_6$(mesitylene)[2] suggested that because of prohibitive non-bonded interactions (ligand–Ph and ligand–CO), larger polyene ligands could not adopt a similar configuration and studies were begun using other 4- and 6-electron donors. This paper deals with a new type of derivative in which a polyene is bound to the three cobalt atoms of the cluster.

RESULTS AND DISCUSSION

Preparation of $PhCCo_3(CO)_6(C_8H_8)$

The complex, $PhCCo_3(CO)_6(1,2\text{-}h^2{:}3,4\text{-}h^2{:}7,8\text{-}h^2\text{-}C_8H_8)$ can be prepared in low yield by two methods [eqns. (1) and (2)]

$$C_8H_8 + PhCCo_3(CO)_9 \xrightarrow[\text{reflux}]{\text{ether}} PhCCo_3(CO)_6(C_8H_8) + 3\ CO \qquad (1)$$

$$C_8H_8 + PhCCo_3(CO)_6(\text{arene}) \rightarrow PhCCo_3(CO)_6C_8H_8 + \text{arene} \qquad (2)$$

The dark brown compound sublimes at 40° but only with considerable decomposition, and reverts back rapidly to $PhCCo_3(CO)_9$ by reaction with atmospheric CO. It is unstable at 20° in solutions that do not contain an excess of ligand, decomposing to

---

* For Part VI see ref. 1.

an uncharacterised brown precipitate and $PhCCo_3(CO)_9$. Likewise, decomposition rather than protonation of the COT occurs in conc. H_2SO_4. Lewis bases displace the COT to give the derivatives, $PhCCo_3(CO)_{9-x}L_x$, described earlier[3].

Analogous $YCCo_3(CO)_6(C_8H_8)$ derivatives ($Y=CH_3$ and F) could not be isolated under similar reaction conditions or at lower temperatures but two as yet uncharacterised brown air-sensitive compounds which appear to have terminal and triply-bridging carbonyl groups and rigid COT ligands, are formed at higher reaction temperatures [also from $PhCCo_3(CO)_9$].

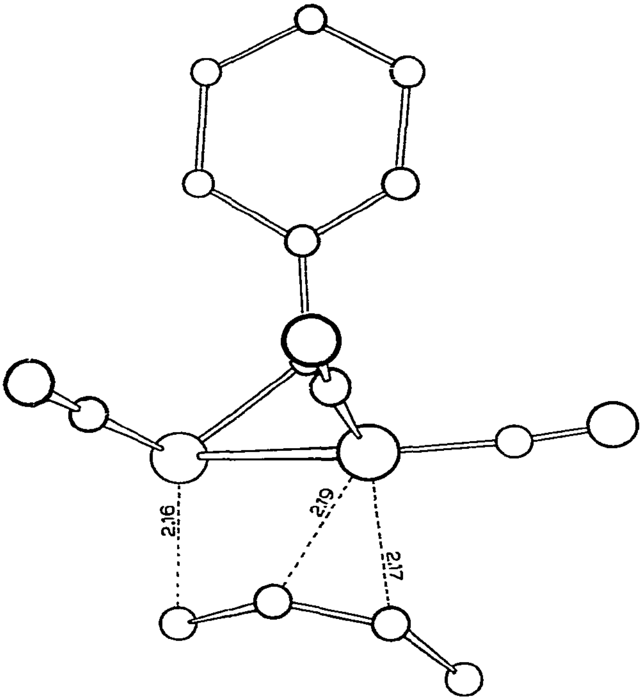


Fig. 1. Structure of $PhCCo_3(CO)_6C_8H_8$.

Structure of $PhCCo_3(CO)_6(C_8H_8)$

An X-ray analysis[2] of $PhCCo_3(CO)_6(C_8H_8)$ revealed that the COT has replaced the three carbonyl groups in axial positions in $PhCCo_3(CO)_9$ and is co-ordinated to *three* cobalt atoms (Fig. 1). In assuming its position below the basal triangle the C_8H_8 ring has retained the tub conformation of the free ligand and one carbon–carbon bond is essentially a free double bond having little interaction with the cluster[4]. It appears that the $Co_3–C_{apical}$ bond (1.85 Å) is significantly shorter than the corresponding bonds to the other cobalt atoms (1.90 Å). In this context it is noted that Co_3 is uniquely placed with respect to the phenyl ring which is believed to form a delocalised system with the cluster[1,3].

IR and mass spectra

Table 1 lists the $\nu(CO)$ bands. A weak band at 1617 cm^{-1} could be assigned

TABLE 1

IR SPECTRUM OF $PhCCo_3(CO)_6C_8H_8$ (2200–1600 cm^{-1})[a]

Frequency (cm^{-1})	Assignment	Frequency (cm^{-1})	Assignment
2050 m	$\nu(^{12}CO)$	1989 w	$\nu(^{12}CO)$
2022 vs		1983 (sh)	
2017 s		1970 w	$\nu(^{13}CO)$
2010 (sh)		1617 w	$\nu(C{=}C)$

[a] In octane and CCl_4.

to the uncoordinated C=C stretching mode.

The mass spectrum showed the effect of extreme thermal decomposition; even under the most favourable conditions only ions arising from $PhCCo_3(CO)_9$ and C_8H_8 were observed.

PMR spectrum

The PMR spectrum of $PhCCo_3(CO)_6C_8H_8$ at 35° in CS_2 showed three distinct features, (1) characteristic phenyl resonances at 2.22 and 2.74 τ (2) a sharp single peak at 4.36 τ of varying intensity due to uncoordinated C_8H_8 (3) a broad weak peak centred at 5.50 τ spread over 2.5 ppm. Clearly the molecule is exhibiting fluxional behaviour[5] and a series of low temperature spectra were recorded (Fig. 2) which enabled us to deduce the main pathway by which a time-averaged environment was achieved*.

Decomposition of the compound in CS_2 occurred above 15°. This decomposition was minimized by the use of a cyclohexane/$CDCl_3$/C_8H_8 solvent system above this temperature and although this produced added problems from the large ligand peak, a single resonance was detected at 60° at 5.54 τ, close to the weighted mean value of the ligand proton shifts at −20° (5.50 τ). Therefore the frozen species are the same as the rapidly equilibrating species at higher temperatures. This observation, together with the fact that the number and relative intensities of the ν(CO) bands is unchanged over the same temperature range, excludes any possibility that COT rearranges, for example, to a bicyclo derivative.

Uncoordinated C_8H_8 persisted down to 0° but the dissociation is probably slow relative to the intramolecular rearrangement.

$$\begin{tikzcd}
PhCCo_3(CO)_6C_8H_8 \arrow[r, rightleftharpoons, "\text{Dissociation}"] \arrow[d, "\text{Intramolecular rearrangement}"] & PhCCo_3(CO)_6+C_8H_8 \arrow[d] \\
PhCCo_3(CO)_6C_8H_8 & \text{Irreversible decomposition}
\end{tikzcd}$$

This facile dissociation, unusual in COT derivatives, explains the instability of the complex in solution and the efficiency with which it reacts with CO.

The limiting spectrum at −20° is in accord with an instantaneous structure in

---

* These spectra are reproducible and reversible over the temperature range, 15°→−80°.

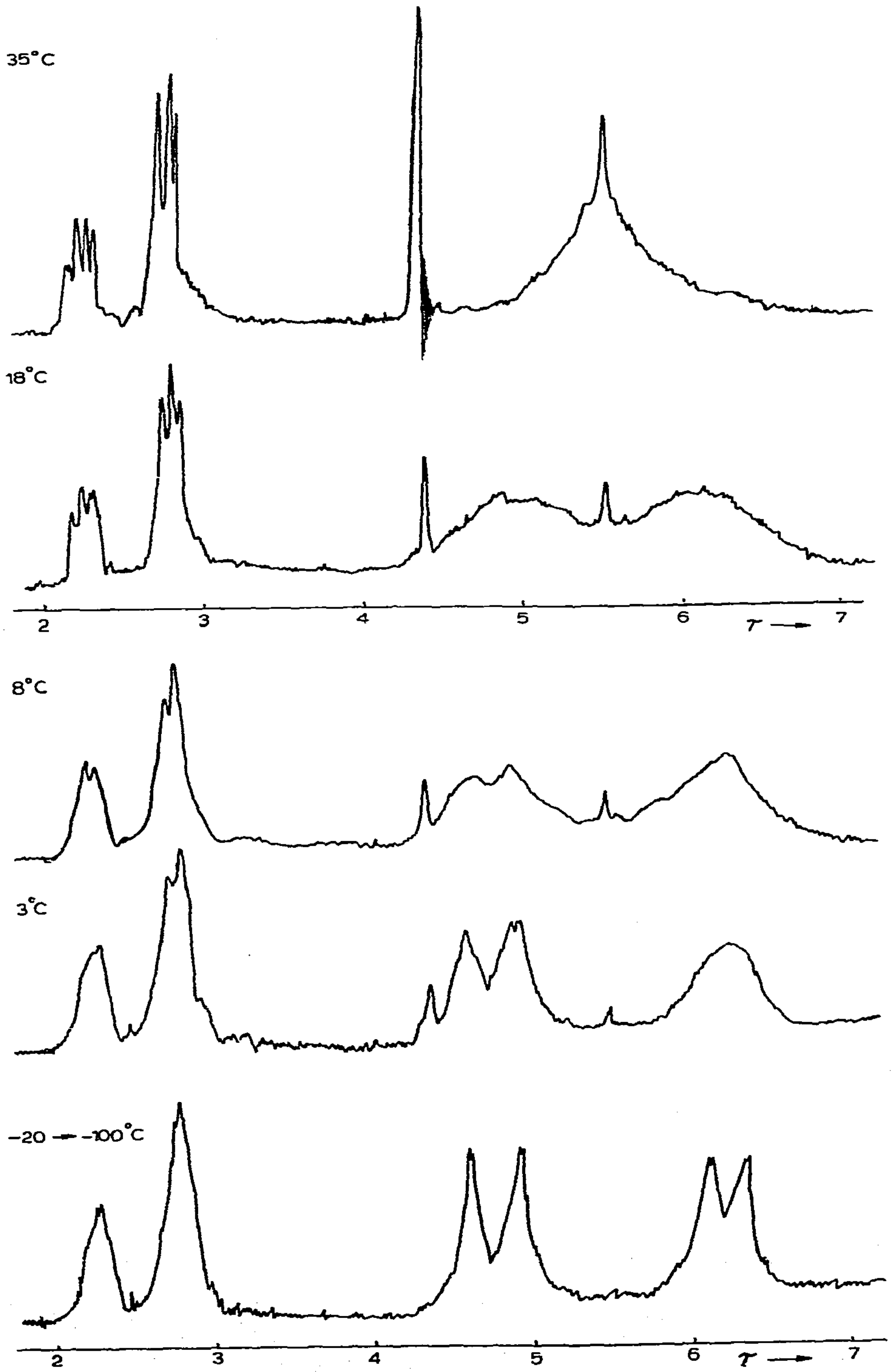
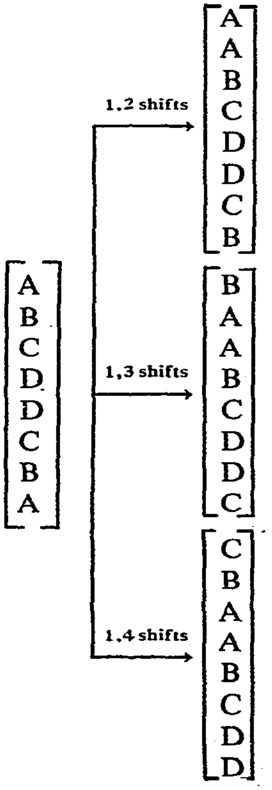


Fig. 2. PMR spectra of $PhCCo_3(CO)_6C_8H_8$ in CS_2.

which there are four equal pairs of hydrogen atoms (protons A,B,C,D defined in Fig. 3) *i.e.* the solid state structure[4]. No spin hyperfine structure which would aid assignment could be resolved, even at very low temperatures where broadening due to the C_8H_8 exchange should be negligible. Nevertheless it is reasonable to assign the two low-field resonances at 4.58 and 4.87 τ to protons D and A, though not necessarily in that order. Resonances due to uncoordinated double bonds in COT complexes normally occur close to the chemical shift for the uncoordinated ligand around 4.5 τ (certainly never as high as 6.13 τ)[6,7] while the assignment for A is based on a comparison with the spectra of a number of polyene complexes[6-8] where H_A protons do not exhibit the characteristic large upfield displacements of H_B or H_C protons. It is not possible to differentiate between the chemical shifts (6.13 and 6.41 τ) for B and C protons and indeed there is no need to in order to establish the predominant pathway for rearrangement.

In principle there are several possible rearrangements which would lead to a time-averaged single-line spectrum; a sequence of (1,2), (1,3), (1,4) or 1,5 shifts of the C_8H_8 moiety relative to the basal Co_3 triangle or a random rearrangement. However the observation (Fig. 2) that the B,C pair of resonances collapse more rapidly than the A,D pair as the temperature rises rules out a random rearrangement. Furthermore, a sequence of 1,5 shifts would average A with D and B with C without leading to a

SCHEME 1



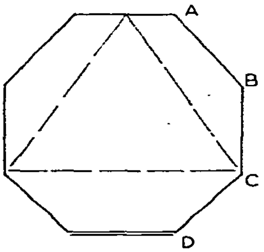


Fig. 3. Orientation of C_8H_8 protons relative to the Co_3 triangle.

single-line spectrum. Scheme 1 illustrates how the protons are permuted among the four environments during a sequence (1,2), (1,3) or 1,4 shifts.

The 1,3 pathway would lead to an initial symmetrical collapse. Both 1,2 and 1,4 shifts have two protons which do not change their environment but only for 1,2 shifts would the B,C pair broaden first. Therefore we suggest that the pathway leading to complete randomization is a sequence of 1,2 shifts, a pathway apparently favoured by a number of fluxional COT molecules[5], although this is the first cluster derivative for which a qualitative analysis has been presented. It should be noted that our analysis requires only that the assignment of proton D is correct, of which there is little doubt. It is possible to estimate from the line separation (using tje equation, $k=2^{-\frac{1}{2}}\pi\cdot\delta\nu$)[9] that $k\approx3.7\times10^2$ sec^{-1} or applying the Gutowsky-Holm method[9] to two lines (D and the average of B,C) $E_A=9.0$ kcal and $\nu_0=7.8\times10^8$ sec^{-1}. Both activation parameters are likely to be an order of magnitude too low because there are more than two spins exchanging[9,10].

It has already been pointed out that a sequence of 1,5 shifts do not lead directly to the equivalence of all protons. The spectrum at 15° indicates that this might be a complimentary process to the 1,2 shifts which ensure complete randomization. It is unfortunate that other $YCCo_3(CO)_9$ clusters do not form analogous derivatives amenable to study but studies are underway to see whether TMCOT derivatives are more stable.

CONCLUSION

At this stage the questions, why does an arene coordinate to one cobalt and COT to three or which configuration is preferred by a 6-electron polyene cannot be answered with certainty. Arenes possibly have no choice because the six-membered rings would be too small to fit under the basal triangle. For the larger polyenes basal attachment lessens intramolecular interactions and this is seen clearly by a comparison of the $PhCCo_3(CO)_6COT$[4] and $CH_3CCo_3(CO)_6$(mesitylene)[2] structures where deformation of the apical group occurs only in the latter compound. The bonding of the two polyenes to the cluster is also different one having a localised the other a delocalised system and it is interesting that the spectral properties of analogous cycloheptatriene derivatives indicate a localised, three-centre attachment[11].

The instability of other methylidynetricobalt COT derivatives follows the pattern observed with all polyene complexes (an explanation for this is given elsewhere[1]) and provides further support for the postulate[3] that the coordination behaviour of $YCCo_3$ clusters is governed by the electronic nature of the apical group.

EXPERIMENTAL

All reactions and manipulations were carried out under nitrogen. Mass and IR spectra were recorded on an AEI MS9 (70 eV) and Perkin–Elmer 225 spectrophotometer respectively. Proton NMR spectra were run on Varian HA 100 and JEOL 60 spectrophotometers with CS_2 as the solvent and TMS as reference.

Preparation of $PhCCo_3(CO)_6C_8H_8$

(*a*). A solution of $PhCCo_3(CO)_9$ (0.5 g) in cyclooctatetrene (3.5 cm^3) and diethyl ether (20 cm^3) was boiled for 6 h. The solvent was removed under reduced pressure and the concentrate diluted with 25 cm^3 hexane, centrifuged and the solution set aside at 0° to crystallize. Small dark crystals of $PhCCo_3(CO)_6(1,2\text{-}h^2{:}3,4\text{-}h^2{:}7,8\text{-}h^2\text{-}C_8H_8)$ were deposited; yield 0.045 g (9 %). (Found: C, 47.01; H, 2.44. $C_{21}Co_3H_{13}O_6$ calcd.: C, 46.85; H, 2.43 %.)

(*b*). (Phenylmethylidyne)hexa*hapto*-*o*-xylenetricobalt hexacarbonyl (0.16 g) was heated with cyclooctatetraene (1 cm^3) at 70–75° for 30 min. The resulting solution was diluted with hexane (20 cm^3) and the complex isolated as described above. Yield, 0.025 g (16 %).

The complex is stable in CO-free air for several weeks but in the presence of CO it rapidly reverts to the parent cluster. In solution this reaction with CO is complete within several minutes. Although the complex dissolves in all common organic solvents the resulting solutions decompose to a brown powder and $PhCCo_3(CO)_9$ very quickly at room temperature even under anaerobic conditions except in the presence of excess COT. For this reason it was not possible to obtain a meaningful molecular weight. The complex dissolved in 98 % H_2SO_4 with some difficulty to give a deep brown solution. An NMR spectrum of this solution suggested the presence of paramagnetic compounds and $CoSO_4$ slowly precipitated.

ACKNOWLEDGEMENT

We are grateful to Dr. Jolley, Massey University, for running the spectra on the JEOL 60 and BASF for the gift of the cyclooctatetraene. One of us (J.L.S.) thanks the N.Z. University Grants Committee for financial assistance.

REFERENCES

1 B. H. Robinson and J. Spencer, *J. Chem. Soc.*, in press.
2 R. J. Dellaca, B. R. Penfold and J. Spencer, *J. Chem. Soc. D*, (1971) 72.
3 T. W. Matheson, B. H. Robinson and W. S. Tham, *J. Chem. Soc.*, in press.
4 J. Spencer, Thesis, Univ. of Otago, 1970.
5 F. A. Cotton, *Accounts Chem. Res.*, 1 (1968) 257.
6 M. L. Maddox, S. L. Stafford and H. D. Kaesz, *Advan. Organometal. Chem.*, 3 (1965) 1.
7 R. B. King, *J. Organometal. Chem.*, 8 (1967) 129.
8 M. A. Bennett, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, (1961) 2037.
9 H. S. Gutowski and C. H. Holm, *J. Chem. Phys.*, 25 (1956) 1228.
10 A. Allerhard, H. S. Gutowsky, J. Jones and R. A. Meinzer, *J. Amer. Chem. Soc.*, 88 (1966) 3185.
11 J. Spencer and B. Hanning, unpublished observations.