# The Synthesis and Nuclear Magnetic Resonance Spectroscopic Study of $[Rh_{10}S(CO)_{22}]^{2-}$ †

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The reaction of $[Rh_4(CO)_{12}]$ with $SCN^-$ in Pr$^i$OH or tetrahydrofuran at atmospheric pressure gives $[Rh_{10}S(CO)_{22}]^{2-}$ in good yield. The reaction is complex and the nature of some of the reaction intermediates is discussed. N.m.r. spectroscopic studies ($^{103}Rh$, $^{13}C$, and $^{13}C-\{^{103}Rh\}$) at low temperature show the solution structure of $[Rh_{10}S(CO)_{22}]^{2-}$ to be entirely consistent with that found in the solid state; at higher temperatures complete fluxionality of *both* the carbonyl and metal polyhedra is found. At 95 °C, conversion into $[Rh_{17}(S)_2(CO)_{32}]^{3-}$ occurs.

Many high-nuclearity carbonyl transition-metal clusters containing main-group interstitial atoms are now known. Some have been prepared under forcing conditions $\{[Rh_9E(CO)_{21}]^{2-}$ (E = P[1] or As[2]), $[Rh_{10}E(CO)_{22}]^{3-}$ (E = P[3] or As[2]), $[Rh_{12}Sb(CO)_{27}]^{3-}$,[4] and $[Rh_{17}(S)_2(CO)_{32}]^{3-}$ [5]$\}$ but many others have been prepared under mild conditions.[6,7]

We now report the synthesis of $[Rh_{10}S(CO)_{22}]^{2-}$ from readily available starting materials under mild conditions. The reaction pathway is complex and the possible nature of some of the intermediates is discussed. The structure in solution at low temperature is found to be identical to that in the solid state, whereas *both* the carbonyl and metal polyhedra are completely fluxional at 60 °C; at 95 °C conversion into $[Rh_{17}(S)_2(CO)_{32}]^{3-}$ occurs.

## Results and Discussion

*Preparation of* $[Rh_{10}S(CO)_{22}]^{2-}$.—The reaction of $[Rh_4(CO)_{12}]$ with $SCN^-$ provides the best single-step synthesis of $[Rh_{10}S(CO)_{22}]^{2-}$. In Pr$^i$OH, $[N(PPh_3)_2]SCN$ reacts with $[Rh_4(CO)_{12}]$ under nitrogen very quickly at room temperature with rapid evolution of carbon monoxide and within minutes there is a black precipitate (*ca.* 85% yield) of essentially $[N(PPh_3)_2]_2[Rh_{10}S(CO)_{22}]$ contaminated mainly with a little $[N(PPh_3)_2][Rh_3S_2(CO)_6]$; ‡ the pure product can be obtained in *ca.* 60% yield by fractional recrystallization from tetrahydrofuran (thf)–Pr$^i$OH.

A much slower reaction occurs on carrying out the reaction in thf with KSCN at room temperature. In this case, the product does not precipitate and it is possible to monitor the course of the reaction by i.r. spectroscopy. In this way it has been possible to recognize, after the initial formation of other very unstable species which are presently under investigation, the formation of $[Rh_5(CO)_{15}]^-$ [8] and $[Rh_5(CO)_{14}(SCN)]^{2-}$.[9] These two species, however, are only stable under carbon monoxide and, as a result, there is further reaction under a nitrogen atmosphere to give $[Rh_{10}S(CO)_{22}]^{2-}$. In order to confirm the involvement of pentanuclear clusters in the formation of $[Rh_{10}S(CO)_{22}]^{2-}$, we treated $[Rh_5(CO)_{15}]^-$ with $[Rh_5(CO)_{14}(SCN)]^{2-}$ (1 : 1) in thf under a nitrogen atmosphere at room temperature and found the main product to be $[Rh_{10}S(CO)_{22}]^{2-}$. It seems probable that cleavage of the S–C bond occurs at this stage because *X*-ray data on $[Rh_5(CO)_{14}(SCN)]^{2-}$ [9] show the thiocyanate to be *S*-bonded to the apical rhodium atom, which is the same stereochemistry found for $[Rh_5(CO)_{14}I]^{2-}$.[10]

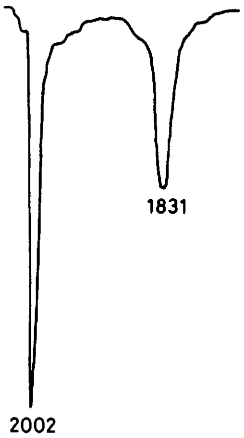

**Figure 1.** I.r. spectrum (cm$^{-1}$) of $[N(PPh_3)_2]_2[Rh_{10}S(CO)_{22}]$ in thf

A previous route to $[Rh_{10}S(CO)_{22}]^{2-}$ used the slow decomposition of $[Rh_6(CO)_{14}(SCN)_2]^{2-}$.[11] Such disubstituted hexanuclear clusters are generally unstable and could well involve decomposition *via* formation of pentanuclear clusters and mononuclear fragments.

*Spectroscopic Measurements*.—The i.r. spectrum of $[Rh_{10}S(CO)_{22}]^{2-}$ in thf is shown in Figure 1. Although the position of the terminal carbonyl band (2 002 cm$^{-1}$) is very similar to that found for $[Rh_{17}(S)_2(CO)_{32}]^{3-}$, $[Rh_{10}S(CO)_{22}]^{2-}$ can be distinguished from $[Rh_{17}(S)_2(CO)_{32}]^{3-}$ since it shows only one band in the bridging region (1 831 cm$^{-1}$) (Figure 1) whereas $[Rh_{17}(S)_2(CO)_{32}]^{3-}$ has two equally intense bands (1 840 and 1 805 cm$^{-1}$ in thf).

Consistent with the solid-state structure[11] (Figure 2), direct $^{103}Rh$ n.m.r. measurements on $[N(PPh_3)_2]_2[Rh_{10}S(CO)_{22}]$ in thf at −70 °C show two resonances at −738.6 and −1 154.9 p.p.m. in the ratio 1 : 4 due to the square-capping rhodium

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† Dodeca-μ-carbonyl-decacarbonyl-μ$_{10}$-thio-decarhodate(2−).

‡ Preliminary *X*-ray studies show that the structure of $[Rh_3(\mu_3-S)_2(CO)_6]^{2-}$ consists of a $Rh_3$ triangle capped on both sides by face-bridging sulphides and each rhodium has two terminal carbonyls above and below the metal triangle.

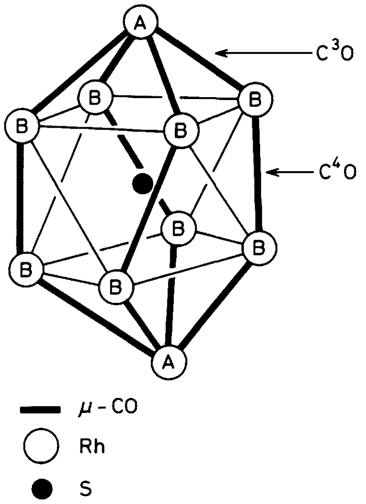
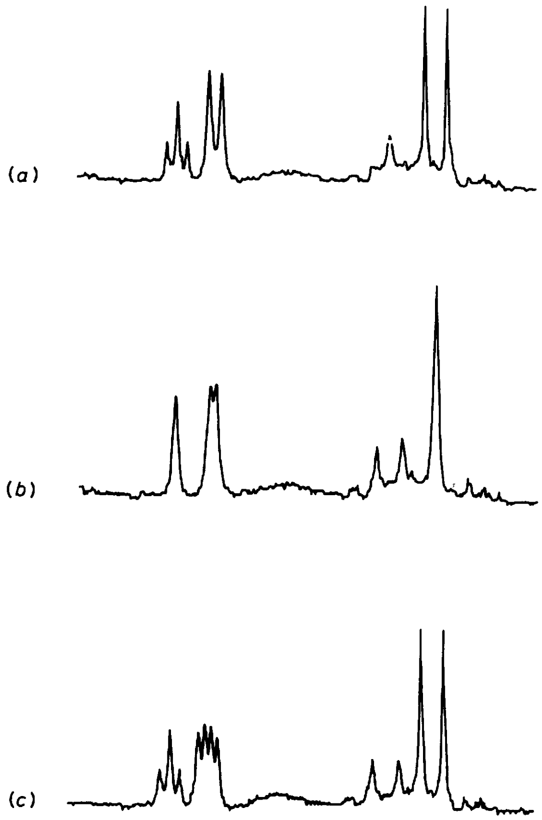


**Figure 2.** Schematic representation of the *X*-ray structure of $[Rh_{10}S(CO)_{22}]^{2-}$.[13] For clarity, the two sets of terminal carbonyls ($Rh_A$–$C^1O$ and $Rh_B$–$C^2O$) have been omitted (see text)



| Assignment | 4 | 3 | 1 | 2 |
|---|---|---|---|---|
| $\delta(^{13}CO)$/p.p.m. | 236·9 | 230·8 | 200·3 | 192·5 |
| $^1J$(Rh - CO)/Hz | 42·7 | 55·0<br>27·5 | 109·9 | 94·6 |

**Figure 3.** $^{13}C\text{-}\{^{103}Rh\}$ N.m.r. spectra of $[N(PPh_3)_2]_2[Rh_{10}S(CO)_{22}]$ (*ca.* 25% $^{13}CO$) in thf at −82 °C: (*a*) decoupling at 3.156 317 MHz [$\delta(^{103}Rh_A)$ = −1 169.1 p.p.m.]; (*b*) decoupling at 3.157 627 MHz [$\delta(^{103}Rh_B)$ = −754.7 p.p.m.]; and (*c*) non-decoupled spectrum

atoms, $Rh_A$, and square-antiprismatic rhodium atoms, $Rh_B$. The $^{13}C$ and $^{13}C\text{-}\{^{103}Rh\}$ n.m.r. spectra at −82 °C are shown in Figure 3 and are also entirely in accord with the solid-state structure which shows that each rhodium has one terminal carbonyl ($Rh_A$–$C^1O$ and $Rh_B$–$C^2O$ in the ratio 1 : 4 respectively) and two sets of bridging carbonyls [$Rh_A(C^3O)Rh_B$ and $Rh_B(C^4O)Rh_B$] in the ratio 2 : 1 respectively. Thus, decoupling $Rh_A$ [Figure 3(*a*)] causes the doublet at 200.3 p.p.m. due to $C^1O$ to collapse to a singlet and the doublet of doublets due to the asymmetric bridging carbonyl $C^3O$ at 230.8 p.p.m. to become a doublet. Similarly, decoupling $Rh_B$ [Figure 3(*b*)] causes the intense doublet at 192.5 p.p.m. due to $C^2O$ to collapse to a singlet, the resonance at 230.8 p.p.m. due to $C^3O$ to become a doublet, and the triplet at 236.9 p.p.m. due to $C^4O$ to become a singlet. Warming this solution results in the simultaneous broadening of all these resonances and at 60 °C a symmetrical, but rather poorly resolved, multiplet is observed {$\delta(^{13}CO)$ = 214.6 p.p.m. [calc. $\delta(^{13}CO)_{mean}$ = 215.2 p.p.m.], $^1J(^{103}Rh\text{–}^{13}CO)$ = 8.8 Hz} which collapses to a singlet on irradiation at a single rhodium resonance frequency [$\Xi$ 3.156 887 MHz, $\delta(^{103}Rh_{A,B})$ = −989 p.p.m.]. This shows that there is complete fluxionality of *both* the carbonyl and metal polyhedra at this temperature and is thus identical to the behaviour of $[Rh_{10}E(CO)_{22}]^{3-}$ (E = P or As) at high temperature.[12] For $[Rh_{10}P(CO)_{22}]^{3-}$, complete fluxionality of the metal skeleton has been shown to occur by $^{31}P$ n.m.r. measurements. At 75 °C, the 40.5-MHz $^{31}P$ n.m.r. spectrum consists of a symmetrical undecet resulting from a fluxional metal skeleton with $J(^{103}Rh_A\text{–}^{31}P) = J(^{103}Rh_B\text{–}^{31}P)$ = 31.7 Hz whereas at −80 °C a triplet of nonets is found because the metal skeleton is now static with $J(^{103}Rh_A\text{–}^{31}P)$ = 21 and $J(^{103}Rh_B\text{–}^{31}P)$ = 56 Hz.[12] For $[Rh_{10}As(CO)_{22}]^{3-}$, the $^{13}C$ n.m.r. spectrum at 91 °C consists of a well resolved symmetrical undecet [$J(^{103}Rh_{A,B}\text{–}^{13}CO)$ = 9.3 Hz], which arises from coupling to equivalent rhodium atoms, and, on irradiation at a single rhodium frequency, $\Xi$ 3.156 922 MHz [$\delta(^{103}Rh_{A,B})$ = —972 p.p.m.], collapses to a singlet.[12] However, it was not possible to obtain better resolved spectra on $[Rh_{10}S(CO)_{22}]^{2-}$ at higher temperatures since further reaction occurred to give $[Rh_{17}(S)_2(CO)_{32}]^{3-}$ as the only observable product in the $^{13}C$ n.m.r. spectrum (after 1 h at 95 °C in EtCN).

As found with other related clusters,[13] the values of $\delta(^{103}Rh)$ for static $[Rh_{10}S(CO)_{22}]^{2-}$ are not very different from those found for the isoelectronic, isostructural clusters, $[Rh_{10}E(CO)_{22}]^{3-}$ [E = As, $\delta(^{103}Rh_A)$ = −495, $\delta(^{103}Rh_B)$ = − 1 220 p.p.m. at −90 °C; E = P, $\delta(^{103}Rh_A)$ = −607, $\delta(^{103}Rh_B)$ = −1 281 p.p.m. at −70 °C],[12] and it seems probable that the increased charge on going from the di- to the tri-anion is mainly dissipated onto the carbonyl ligands as reflected by the mean carbonyl chemical shift moving to lower field with increased charge on the anion [$\delta(^{13}CO)_{mean}$ = 215.2, 220.2, and 219.4 p.pm. for E = S, P, and As respectively]. It should also be noted that the value of $^1J(Rh_A\text{–}C^1O)$ (109.9 Hz) is higher than is normally found. Similar high values have also been found in $[Rh_7(CO)_{16}]^{3-}$,[14] $[Rh_{10}P(CO)_{22}]^{3-}$,[12] and $[Rh_{14}(CO)_{25}H_{4-n}]^{n-}$ (*n* = 3 or 4) [13] and it appears as though they are always associated with either triangular- or square-face capping Rh–CO groups in which the carbonyl group is exactly aligned with the centre of the metallic skeleton.

This study provides another example of a metal polyhedral rearrangement, which has previously been found in $[Pt_n(CO)_{2n}]^{2-}$ (*n* = 3 or 4),[15] $[Rh_9P(CO)_{21}]^{2-}$,[16] $[FeRu_3(CO)_{12}H_2L]$ (L = $PMe_2Ph$ or $PMe_3$),[17] and $[FeRu_3(CO)_{11}H_2L_2]$ [L = $PMe_3$, $PPh_3$, $P(OMe)_3$, or $P(OEt)_3$] [17] and suggests that such rearrangements, which could be important in surface reconstruction on metals, may be quite widespread.

## Experimental

The $^{103}$Rh, $^{13}$C, and $^{13}$C-{$^{103}$Rh} n.m.r. measurements were carried out as described previously.[18] For $\delta(^{103}Rh)$, 0 p.p.m. $\equiv$ 3.16 MHz at such magnetic field that the protons in $SiMe_4$ resonate at exactly 100 MHz; shifts to high frequency are positive. I.r. measurements were carried out on a Perkin-Elmer 297 spectrometer and a Nicolet MX-1 interferometer using $CaF_2$ i.r. cells. Enrichments with $^{13}CO$ (*ca.* 25%) were carried out on $[N(PPh_3)_2]_2[Rh_{10}S(CO)_{22}]$ in thf solution by direct exchange using standard vacuum-line techniques and all preparations were carried out under a nitrogen atmosphere using Schlenk-tube techniques.

The complexes $[Rh_5(CO)_{15}]^-$ and $[Rh_4(CO)_{12}]$ were prepared as described in the literature.[8,19]

$[N(PPh_3)_2]_2[Rh_{10}S(CO)_{22}]$.—To a suspension of $[Rh_4(CO)_{12}]$ (1.25 g, 1.67 mmol) in Pr$^i$OH (40 cm$^3$) under nitrogen was added $[N(PPh_3)_2]SCN$ (1.01 g, 1.67 mmol). The mixture was stirred for 1 h. The resulting black precipitate was collected by filtration, washed with Pr$^i$OH (2 × 10 cm$^3$), and recrystallized from thf–Pr$^i$OH by slow diffusion, yield 1.12 g (60%). The compound is soluble and stable for prolonged periods in dry thf and EtCN, but is slowly transformed into $[Rh_{17}(S)_2(CO)_{32}]^{3-}$ in acetone, damp solvents, or in the presence of oxygen (Found: C, 40.25; H, 2.15; N, 1.00; Rh, 36.9. $C_{94}H_{60}N_2O_{22}P_4Rh_{10}S$ requires C, 40.95; H, 2.15; N, 1.00; Rh, 37.4%).

The potassium salt was obtained from the reaction of $[Rh_4(CO)_{12}]$ (0.748 g, 1.0 mmol) with KSCN (0.164 g, 1.66 mmol) in thf solution (20 cm$^3$) at room temperature for 18 h. Salts containing other cations $[NMe_4^+$, $NEt_4^+$, or $NMe_3(CH_2Ph)^+]$ were obtained by dropwise addition of the above solution to a stirred aqueous solution containing the bulky cation. For the larger cations there was immediate precipitation whereas concentration was necessary in order to induce precipitation of the product containing smaller cations.

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## References

1 J. L. Vidal, W. E. Walker, R. L. Pruett, and R. C. Schoening, *Inorg. Chem.*, 1979, **18**, 129.
2 J. L. Vidal, *Inorg. Chem.*, 1981, **20**, 243.
3 J. L. Vidal, W. E. Walker, and R. C. Schoening, *Inorg. Chem.*, 1981, **20**, 238.
4 J. L. Vidal and J. H. Troup, *J. Organomet. Chem.*, 1981, **213**, 351.
5 J. L. Vidal, R. A. Fiato, L. A. Cosby, and R. L. Pruett, *Inorg. Chem.*, 1978, **17**, 2574.
6 V. G. Albano and S. Martinengo, *Nachr. Chem. Tech. Lab.*, 1980, **28**, 654.
7 P. Chini, *J. Organomet. Chem.*, 1980, **200**, 37.
8 A. Fumagalli, T. F. Koetzle, F. Takusagawa, P. Chini, S. Martinengo, and B. T. Heaton, *J. Am. Chem. Soc.*, 1980, **102**, 1740.
9 G. Ciani and A. Sironi, personal communication.
10 S. Martinengo, G. Ciani, and A. Sironi, *J. Chem. Soc., Chem. Commun.*, 1979, 1059.
11 G. Ciani, L. Garlaschelli, A. Sironi, and S. Martinengo, *J. Chem. Soc., Chem. Commun.*, 1981, 563.
12 B. T. Heaton and J. L. Vidal, unpublished work.
13 B. T. Heaton, C. Brown, D. O. Smith, L. Strona, R. J. Goodfellow, P. Chini, and S. Martinengo, *J. Am. Chem. Soc.*, 1980, **102**, 6175.
14 C. Brown, B. T. Heaton, L. Longhetti, D. O. Smith, P. Chini, and S. Martinengo, *J. Organomet. Chem.*, 1979, **169**, 309.
15 C. Brown, B. T. Heaton, A. D. C. Towl, P. Chini, A. Fumagalli, and G. Longoni, *J. Organomet. Chem.*, 1979, **181**, 233.
16 O. A. Gansow, D. S. Gill, F. J. Bennis, J. R. Hutchinson, J. L. Vidal, and R. C. Schoening, *J. Am. Chem. Soc.*, 1980, **102**, 2449.
17 W. L. Gladfelter, J. R. Fox, J. A. Smegal, T. G. Wood, and G. L. Geoffroy, *Inorg. Chem.*, 1981, **20**, 3223.
18 B. T. Heaton, L. Strona, S. Martinengo, D. Strumolo, R. J. Goodfellow, and I. H. Sadler, *J. Chem. Soc., Dalton Trans.*, 1982, 1159.
19 S. Martinengo, G. Giordano, and P. Chini, *Inorg. Synth.*, 1980, **20**, 209.

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