# Complexes of 1,2-Bis(isopropylseleno)ethane with Chromium, Molybdenum, and Tungsten Carbonyl Complexes: A Conformational Study of a Chelated Selenium Ligand by Nuclear Magnetic Resonance

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The preparation and temperature-dependent $^1$H n.m.r. spectra are reported for new chelated complexes [LM(CO)$_4$] [L = 1,2-bis(isopropylseleno)ethane; M = Cr, Mo, or W]. The well resolved n.m.r. spectra are interpreted by considering total inversion of the five-membered chelate-ring system but without invoking true inversion about the ligand donor atoms.

THERE has been considerable recent interest in the fluxional behaviour of metal chelate complexes, most of these conformational studies involving complexes of 1,2-diaminoethane or related nitrogen-containing ligands.[1] Also reported [2-4] has been the apparent inversion of terminal alkyl groups attached to ligand sulphur atoms, although in these reports there is little mention of phenomena resulting from conformational changes within the chelate ring itself. Although a number of complexes of bidentate selenium ligands have recently been reported,[5-7] no detailed conformational study of these complexes has yet appeared. Abel and Hutson reported [8] the preparation of various sparingly soluble complexes of metal carbonyls with the bidentate selenium ligand 1,2-bis(methylseleno)ethane (L′). Only

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[1] See, for example, C. J. Hawkins, ' Absolute Configuration of Metal Complexes,' Wiley-Interscience, New York, 1971.

[2] P. Haake and P. C. Turley, *J. Amer. Chem. Soc.*, 1967, **89**, 4611.

[3] E. W. Abel, R. P. Bush, F. J. Hopton, and C. R. Jenkins, *Chem. Comm.*, 1966, 58.

[4] R. Walton, *J. Chem. Soc.* (*A*), 1967, 1852.

[5] E. E. Aynsley, N. N. Greenwood, and J. B. Leach, *Chem. and Ind.*, 1966, 339.

[6] N. N. Greenwood and G. Hunter, *J. Chem. Soc.* (*A*), 1967, 1520.

[7] N. N. Greenwood and G. Hunter, *J. Chem. Soc.* (*A*), 1969, 929.

[8] E. W. Abel and G. V. Hutson, *J. Inorg. Nuclear Chem.*, 1969, **31**, 3333.

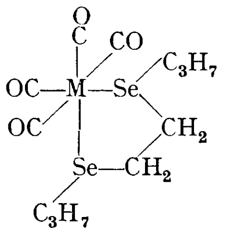
[L'Re(CO)$_3$Cl] was sufficiently soluble to give an n.m.r. spectrum and even this species was too insoluble to permit investigation of the temperature or solvent dependence of the spectra.

The related ligand 1,2-bis(isopropylseleno)ethane, (L), readily forms metal halide complexes which are more soluble than the analogous complexes of L'. This improvement in solubility is also apparent for complexes of L with chromium, molybdenum, and tungsten carbonyls and, at the expense of some additional complexity in their spectra, enabled temperature-dependent n.m.r. studies to be undertaken with these species.

## RESULTS AND DISCUSSION

Only traces of the complexes [LM(CO)$_4$] were obtained by direct action of the ligand on the required metal hexacarbonyl, but displacement of the bidentate hydrocarbon ligand from (bicyclo[2.2.1]heptadiene)tetracarbonylmetal complexes gave reasonable yields of the desired products [equation (1)].

$[M(CO)_4C_7H_8] + C_3H_7Se(CH_2)_2SeC_3H_7 \longrightarrow$



(1)

Chloroform-solution i.r. spectra in the carbonyl region of the complexes are recorded in Table 1. Four absorptions would be expected from the structure shown in equation (1) but only three were actually seen. However, the absorption centred at 1 900 cm$^{-1}$ is broad and would appear to result from two overlapping absorptions. There was no appreciable change in the i.r. spectra between 210 and 333 K. Molecular-weight and conductance measurements indicated that the complexes were neutral monomeric species. Magnetic measurements showed them to be diamagnetic. Temperature-dependent n.m.r. spectra (obtained at 90 MHz) showed that the complexes [LCr(CO)$_4$] and [LMo(CO)$_4$], at least, were stereochemically non-rigid and these spectra are discussed below.

TABLE 1

I.r. stretching bands (cm$^{-1}$) in the metal–carbonyl region

| Complex | CO Band | In CHCl$_3$ | |
|---|---|---|---|
| [LCr(CO)$_4$] | 2 015vs | 1 900br | 1 860 |
| [LMo(CO)$_4$] | 2 012vs | 1 900br | 1 864 |
| [LW(CO)$_4$] | 2 017vs | 1 900br | 1 870 |

*X*-Ray crystallographic studies [9,10] of chelated complexes of sulphur- or selenium-containing ligands indicate that the angles about the donor atoms approach the expected tetrahedral angle with the fourth positions about these atoms presumably occupied by a lone pair of electrons. Thus the chalcogen atoms are centres of asymmetry and the complexes have asymmetry imposed not only by the conformation of the chelate ring but also by the asymmetric ligand atoms. The closest analogues for which conformational studies exist are complexes of *NN'*-dimethylethylenediamine. However, in these studies [11,12] only the symmetric skew conformations were considered, whereas it is now known that the chelate ring is very flexible and not restricted to a pair of enantiomeric skew conformations with $C_2$ symmetry.[1]

The relative stabilities of the various possible molecular conformations may be qualitatively obtained by considering the conformations about the individual single bonds. It is well established that the staggered ethane conformation is preferred over the eclipsed by *ca.* 12 k J mol$^{-1}$. A similar torsional barrier should also exist for the C–Se bond and, while no estimation has been made for the size or shape of the barrier, once again we should expect the staggered conformations to be more stable than the eclipsed. With a large alkyl group attached to the ligand atom the magnitude of this barrier may well be greater than that of the C–C torsional barrier. Neglecting effects arising from non-bonding interactions of the ring substituents, the most favourable arrangements for the five-membered ring system would obviously be the two ($\lambda$ and $\delta$) symmetric skew conformations (ggg) * with *gauche* rotamers about the C–C and both C–Se bonds. Slightly less favourable would be those arrangements with one fully, or partly eclipsed, and two staggered rotamers, either with the C–C bond and one C–Se bond staggered and the other C–Se bond eclipsed (gge), or with both C–Se bonds staggered and the C–C bond eclipsed (geg). These two latter arrangements require that the C–C bond be markedly displaced from the SeMSe plane and they include asymmetric envelope conformations in addition to geg which possesses a reflection plane.

The isopropyl substituents on the chelated ring possess pseudo-axial or -equatorial character and additionally may be projected on the same side (*syn*) or on different sides (*anti*) of the ring. For the *anti*-system account must be taken of the helicities imposed by the relative orientations of the isopropyl groups and this results in ten possible conformations which consist of the five energetically and geometrically equivalent, but enantiomeric, pairs shown in Figure 1. For the *syn*-system, grossly unfavourable steric interactions between

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* The absolute-configuration nomenclature rules of Cahn *et al.*[13] are of limited utility when applied to the distribution of chelate rings as the symbols used to denote a particular conformation depend on the ring substituents and do not specify the ring conformation by itself. We have therefore adopted the system previously used [9] to describe the configuration of a 1,2-bis(methylthio)ethane complex.

[9] D. Britnell, M. G. B. Drew, G. W. A. Fowles, and D. A. Rice, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 501.

[10] H. J. Whitfield, *J. Chem. Soc.* (*A*), 1970, 113.

[11] P. Haake and P. C. Turley, *J. Amer. Chem. Soc.*, 1969, **90**, 2293.

[12] F. F. L. Ho and C. N. Reilly, *Analyt. Chem.*, 1969, **41**, 1835.

[13] R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem. Internat. Edn.*, 1966, **5**, 385.

the bulky isopropyl groups reduce the total to only five possible conformations which include two enantiomeric pairs [λ(ggg), δ(ggg); λ(gge), δ(egg)]. These are shown in Figure 2. In optically inactive solvents the components of an enantiomeric pair are of course n.m.r. indistinguishable.

*N.m.r. Spectra.*—The 90 MHz proton n.m.r. spectra were obtained using both acetone and chloroform solutions, those from acetone being better resolved than those from chloroform. Spectra of the complexes [LCr(CO)$_4$] and [LMo(CO)$_4$] were very similar and that of the latter dissolved in (CD$_3$)$_2$CO is shown in Figures 3 and 4. Whatever the solvent, the spectra at 330 K were similar to that of the free ligand[6] and obviously showed the effects of time-averaging, the signal due to the methylene protons appearing as a singlet and those due to the terminal isopropyl groups appearing as an AX$_6$ spectrum consisting of a septuplet (methine proton) and a sharp, high-field doublet (methyl protons). At 300 K the isopropyl signals were still resolved though the signal due to the methylene protons was now very broad, while below room temperature the well resolved spectra emerged. Coalescence temperatures and $\Delta G_0^\ddagger$ values calculated therefrom are recorded in Table 2. Spectra were obtained at 10 K intervals between 215 and 265 K and it was found that the separation of features (C),(D) and (F),(G) was temperature dependent and reached the maximum values recorded in Table 2. In the case of the complex [LMo(CO)$_4$] dissolved in chloroform this separation did not reach a maximum value within the temperature range examined. Using the INDOR technique, absorptions (C), (D), (F), and (G) were found to be coupled together but none of these was found to be coupled to any other feature in the spectrum.

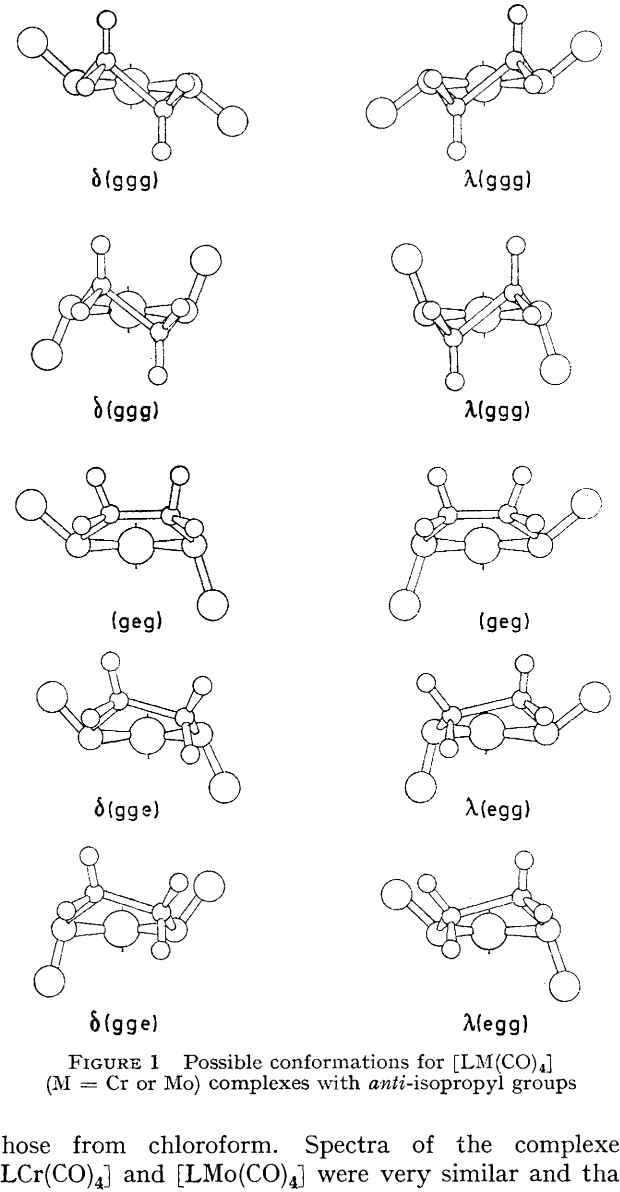

FIGURE 1 Possible conformations for [LM(CO)$_4$] (M = Cr or Mo) complexes with *anti*-isopropyl groups

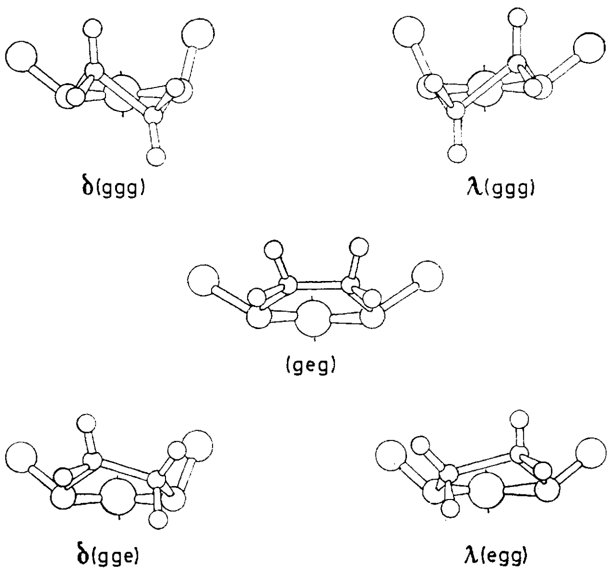

FIGURE 2 Possible conformations for [LM(CO)$_4$] (M = Cr or Mo) complexes with *syn*-isopropyl groups

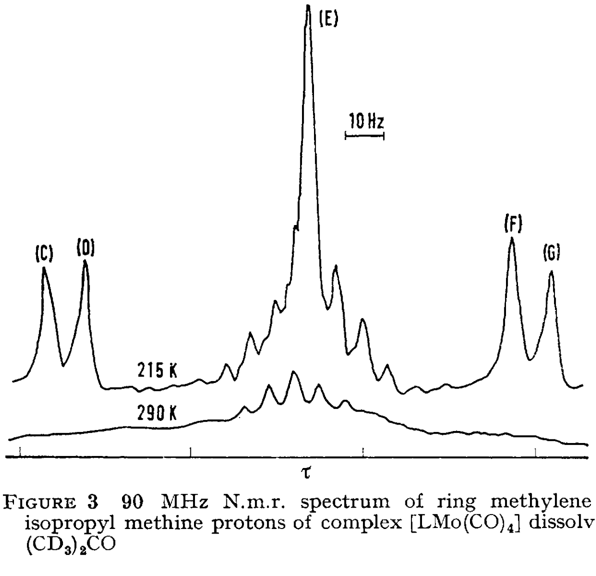

FIGURE 3 90 MHz N.m.r. spectrum of ring methylene and isopropyl methine protons of complex [LMo(CO)$_4$] dissolved in (CD$_3$)$_2$CO

We have assigned absorptions (C),(D) and (F),(G) to the AA′BB′ multiplet arising from the differently shielded axial and equatorial protons of a (ggg) system, the four peaks being envelopes covering some of the more intense unresolved absorptions of what should have been a 24-line spectrum. By analogy with complexes of 1,2-diaminoethane [14] it is probable that the downfield components [(C),(D)] can be assigned to the equatorial protons. As the complexes were diamagnetic ($\chi_g$ values recorded in Table 3), the relatively large chemical shifts cannot be attributed to contact-shift phenomena and their magnitudes possibly result from a small amount of metal–selenium double bonding giving disproportionately large anisotropic effects. The temperature dependence of the chemical shift must result from the intraconversion of equatorial and axial protons which, at higher temperatures, occurs so rapidly as to give a time-averaged signal. Solvent effects would appear to be unimportant as chemical shifts and coalescence temperatures were very similar whatever the solvent. Moreover, in the $(CD_3)_2CO$ solvent there was a small amount of $(CD_3)(CD_2H)CO$ impurity, the signal from which did not shift or broaden on either dissolution of the complexes or on lowering the temperature of the solutions.

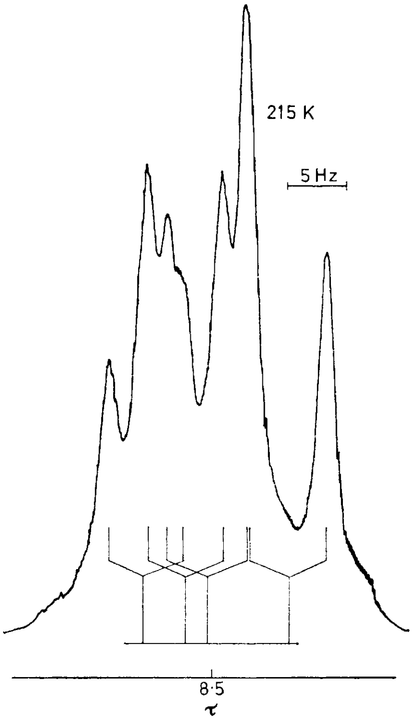

FIGURE 4 90 MHz N.m.r. isopropyl methyl proton spectrum of the complex $[LMo(CO)_4]$ dissolved in $(CD_3)_2CO$

TABLE 2

90 MHz N.m.r. data for the complexes

| Complex | Solvent | Max separation of methylene axial/equatorial proton absorptions (Hz) | Coalescence temp. K | $\Delta G^{\ddagger}$ kJ mol$^{-1}$ |
|---|---|---|---|---|
| $[LCr(CO)_4]$ | $(CD_3)_2CO$ | 141·0 | 300 | 59·1 |
| $[LCr(CO)_4]$ | $CDCl_3$ | 117·0 | 290 | 57·4 |
| $[LMo(CO)_4]$ | $(CD_3)_2CO$ | 121·5 | 295 | 58·4 |
| $[LMo(CO)_4]$ | $CDCl_3$ | | 285 | 56·4 |
| $[LW(CO)_4]$ | $CDCl_3$ | 291·0 | | |

TABLE 3

Molecular weights, molar conductances (in MeCN), and magnetic susceptibilities for the complexes

| Complex | *M* | $\lambda/\Omega^{-1}$ cm$^2$ | $\chi_g$/c.g.s.u. |
|---|---|---|---|
| $[LCr(CO)_4]$ | 405 | 12 | $-0{\cdot}48 \times 10^{-6}$ |
| $[LMo(CO)_4]$ | 467 | 7 | $-0{\cdot}52 \times 10^{-6}$ |
| $[LW(CO)_4]$ | 575 | 10 | $-0{\cdot}44 \times 10^{-6}$ |

The apparent singlet (E) had a half-height linewidth of *ca.* 3 Hz at 215 K and remained in the same position relative to absorptions (C),(D) and (F),(G) whatever the temperature. The intensity of (E) was estimated by subtracting the intensity of the isopropyl methine signal (1/6 that of the isopropyl methyls) from the total intensity of (E + isopropyl methine) and it was found that the ratios of its intensity compared with the sum of the intensities of (C), (D), (F), and (G) remained almost temperature invariant at *ca.* 1 : 1·5 for $[LCr(CO)_4]$ and 1 : 1·7 for $[LMo(CO)_4]$. Any fine structure which may have been associated with (E) could not with certainty be distinguished from the overlapping isopropyl methine proton signals. Similar features which occur in the spectra of complexes $[LPdX_2]$ do have resolvable fine structure and have been assigned to the eclipsed methylene protons of an envelope (geg) conformation.[15] A similar assignment can probably be made for the complexes $[LCr(CO)_4]$ and $[LMo(CO)_4]$. An alternative explanation may be that, as a result of lone-pair inversion about the ligand atoms, a mixture of *syn-* and *anti*-configurations was present in which one of the configurations was the more fluxional and hence gave a time-averaged signal. In principle, this time-averaged signal should also have the fine structure of an AA′BB′ multiplet arising from intrinsic non-equivalence of the geminal methylene protons attached to a chiral centre. However, the presence of two identical chiral centres in the molecule and the possibility of internal compensation would probably result in a very small intrinsic non-equivalence,[16] small values of $\Delta\nu/J$, and hence an apparent singlet. A serious objection to the assignment of (E) to a time-averaged signal is that, under these circumstances, the signal would be expected to broaden as the temperature was lowered and no such additional broadening was detected.

At low temperatures the isopropyl methyl proton spectra of the complexes $[LCr(CO)_4]$ and $[LMo(CO)_4]$ appeared as four overlapping doublets with a common coupling constant of 6·7 Hz. Although the possibility

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[14] J. L. Sudmeier and G. L. Blackmer, *Inorg. Chem.*, 1971, **10**, 2010.

[15] G. Hunter and R. C. Massey, *J.C.S. Chem. Comm.*, 1973, **797**.

[16] L. M. Jackman and S. Sternhell, ‘ Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,’ 2nd edn., Pergamon, Oxford, 1969, p. 375.

of accidental equivalence could not with certainty be eliminated, the similar linewidths of all the components suggested that this was improbable and that the actual number of doublets was as observed. In principle there should be two methyl doublets for each isopropyl group attached to a chiral centre. However, the presence of the two identical chiral centres in the molecule may once again cause any intrinsic non-equivalence to be too small to be resolvable, thus giving only one methyl doublet per isopropyl group. In view of the methylene proton spectrum, we consider the only plausible combinations of conformations which would give the required number of doublets to be either: (*a*) with two doublets per isopropyl group, a combination of time-averaged *syn*-configuration and either *anti*-δ(ggg) or -λ(ggg) conformations; or (*b*) with only one doublet per isopropyl group, a combination of *anti*-δ(ggg), -λ(ggg), and -(geg) conformations. Case (*a*) suggests that coalescence in the spectra represents *syn* ◄► *anti* conversion by lone-pair inversion about the selenium atoms, whereas case (*b*) suggests that coalescence represents *anti*-δ(ggg) ◄► *anti*-λ(ggg) intraconversion and hence chelate-ring inversion occurring *via* a meta-stable-intermediate envelope conformation. The almost identical values for $\Delta G_c^\ddagger$ of [LCr(CO)$_4$] and [LMo(CO)$_4$], allied with the lack of additional broadening of absorption (E) at low temperatures, suggest that lone-pair inversion about the ligand atoms was not the observed process and we believe that these n.m.r. spectra are best interpreted in terms of conformational rather than configurational changes.

The spectra of complexes [LCr(CO)$_4$] and [LMo(CO)$_4$] differed considerably from that of [LW(CO)$_4$]. This spectrum, which was almost temperature invariant and persisted at 330 K, is shown in Figure 5. Relative-intensity measurements indicated that peaks (X), (Y), and (Z) could be assigned to the methylene part of the spectrum. Peaks (X) and (Z) were separated by 3·23 p.p.m. and were coupled to each other but to no other part of the spectrum. There were only two overlapping high-field doublets, once again with a common coupling constant of 6·7 Hz. Although less information could be obtained from this spectrum, the ring system was obviously much less flexible than in the case of the corresponding Cr and Mo complexes and any interconversion reaction occurring was obviously slow compared with the n.m.r. time scale. One model which would fit the spectrum has the selenium lone pair almost fully involved in the metal–selenium bonding with the bond angles about the donor atoms approaching 120°. This would still allow the two enantiomeric λ and δ symmetric skew conformations with the equatorial methylene protons presumably experiencing even greater anisotropic effects. The closely spaced doublet (Y) could be assigned to the eclipsed methylene protons of an intermediate envelope conformation with the two carbon atoms only slightly displaced from the MSe$_2$ plane leaving some residual effects due to anisotropy. Only two types of isopropyl group would be required for this model.

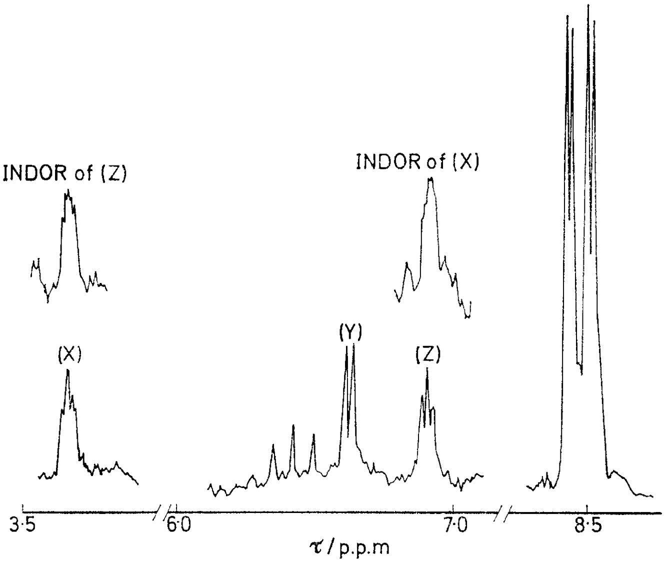

FIGURE 5 90 MHz N.m.r. spectrum of (LW(CO)$_4$] dissolved in (CD$_3$)$_2$CO

## EXPERIMENTAL

1,2-Bis(isopropylseleno)ethane was prepared as previously described.[5]

*Interaction of* 1,2-*Bis*(*isopropylseleno*)*ethane with* (*Bicyclo*-[2.2.1]*heptadiene*)*tetracarbonylmetal*.—The requisite carbonyl complex (*ca.* 0·5 g) was heated under reflux for 30 min in n-heptane with the stoicheiometric amount of 1,2-bis(isopropylseleno)ethane. After cooling the solvent was evaporated off and the residue recrystallised three times from hexane to give yellow crystals of [1,2-bis(isopropylseleno)-ethane]tetracarbonylmetal (Found: C, 33·9; H, 4·3. Calc. for $C_{12}H_{18}CrO_4Se_2$: C, 33·6; H, 4·2. Found: C, 30·2; H, 3·7. Calc. for $C_{12}H_{18}MoO_4Se_2$: C, 30·5; H, 3·8. Found: C, 26·2; H, 3·3. Calc. for $C_{12}H_{18}O_4Se_2W$: C, 25·7; H, 3·2%).

N.m.r. spectra were obtained using a Bruker HX 90 spectrometer.

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