Conformational Studies of Chelated Sulphur- and Selenium-containing Ligands by Nuclear Magnetic Resonance. Part II.[1] Complexes of 1,3-Bis(methylseleno)-2,2-dimethylpropane with Chromium, Molybdenum, and Tungsten Carbonyl Complexes

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The preparation of the new chelated complexes $[(\mathrm{msdp})\mathrm{M(CO)}_4]$ [msdp = 1,3-bis(methylseleno)-2,2-dimethylpropane; M = Cr, Mo, or W] and their temperature-dependent ^{1}H n.m.r. spectra are reported. The well-resolved n.m.r. spectra are interpreted by considering total inversion of the six-membered ring system and thermodynamic parameters, obtained by n.m.r. line-shape fitting techniques, are reported for the ring inversions.

ALTHOUGH the conformational analysis and confirmatory experimental studies for organic alicyclic molecules are well-established, those of inorganic chelate complexes, which can be regarded essentially as highly substituted heterocyclic systems, are still relatively undeveloped. Theoretical studies of conformational processes occurring in chelate complexes of nitrogen-containing ligands have recently appeared[2,3] but it is already apparent that the barriers to ring inversion in these complexes are so low as to render unrewarding confirmatory low-temperature n.m.r. studies. Much more promising would seem to be studies of complexes of heavier ligand atoms such as phosphorus, arsenic, sulphur, and selenium, as their presence should stiffen the chelate ring, causing much higher ring-inversion barriers, and thus permitting full n.m.r. spectral analyses. However, with reference to the latter two ligand atoms there continues some uncertainty as to the exact cause of the well-established coalescence phenomena which occur in the temperature-dependent n.m.r. spectra of their complexes.

We have recently reported[1,4] n.m.r. spectral studies of five-membered chelate complexes of the ligand, 1,2-bis(isopropylseleno)ethane, and considered that coalescence phenomena occurring in their spectra were better interpreted in terms of conformational changes arising from ring inversion than of configurational changes resulting from lone-pair inversion about the ligand atoms. Other workers have since reported[5] similar studies of palladium(II) and platinum(II) complexes of diethyl selenide and 1,2-bis(ethylseleno)ethane for which they have invoked lone-pair inversion to explain the apparently comparable $\Delta G^{\ddagger}_{c}$ values obtained for complexes of unidentate and bidentate ligands containing the same ligand atom. To derive their values for $\Delta G^{\ddagger}_{c}$, these workers used the well-known relationship based on the signal separation $(\nu_A - \nu_B)$ and the exchange rate k_c, the rate that just results in a coalescence of the A and B signals into a single, rather broad, flat-topped resonance;

$$k_c = \pi(\nu_A - \nu_B)/\sqrt{2}$$

This relationship is applicable only for cases in which the populations of the two forms are exactly equal and where $(\nu_A - \nu_B)$ is large compared with the half-height line-widths of the signals, conditions unlikely to be other than coincidentally fulfilled for these chelate complexes where the studied coalescence was of signals attributable to the terminal alkyl groups attached to the selenium ligand atoms. Therefore these published thermodynamic parameters are of questionable value in resolving the question as to whether conformational or configurational changes are responsible for coalescence phenomena in the spectra of the chelate complexes. Moreover, the apparent *trans*-effect noticed in the complexes when the balancing ligands were changed from chloride to iodide, and used by these authors as an argument to support lone-pair inversion, could equally well be used as evidence to support chelate ring inversion which can be regarded as a series of individual bond rotations and should thus be markedly affected by details of the metal-ligand bonding.

Reliable values for the entropy of activation, $\Delta S^{\ddagger}$, offer some hope of resolving this ambiguity as it is difficult to envisage a non-zero value for this quantity for a system undergoing lone-pair inversion *via* the mechanism proposed by Haake and Turley.[6] The only reliable method for obtaining $\Delta S^{\ddagger}$ values from n.m.r. spectra is by the use of full line-shape fitting techniques,[7] but even then, the small separations of the terminal alkyl group signals make this difficult. We believe that the coalescences of the signals of the bridging methylene protons, with their much larger separations, are much more likely to be informative. However, it is self-defeating to attempt to obtain full thermodynamic parameters for systems too complicated to permit full spectral analysis even under favourable circumstances, and we consider that four is the maximum number of close-coupled bridging methylene protons for which it is possible to obtain reliable information. Accordingly, we have initiated a program of ligand design directed towards the synthesis of complexes which have no more, and preferably less, than four close-coupled bridging methylene protons, and whose n.m.r. spectra should permit of full analysis.

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[1] Part I, R. Donaldson, G. Hunter, and R. C. Massey, *J.C.S. Dalton*, **1974**, 288.

[2] J. R. Gollogly and C. J. Hawkins, *Inorg. Chem.*, 1972, **11**, 156.

[3] L. J. DeHayes and D. H. Busch, *Inorg. Chem.*, 1973, **12**, 1505.

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

[5] R. J. Cross, T. H. Green, and R. Keat, *J.C.S. Chem. Comm.*, **1974**, 207.

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

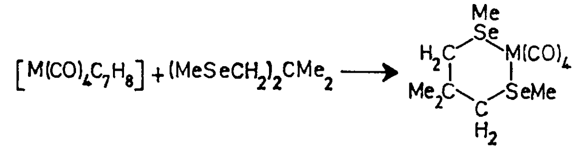
[7] I. O. Sutherland, *Ann. Reports N.M.R. Spectroscopy*, 1971, **4**, 105.

As our first successful example of this approach, we now report reliable thermodynamic parameters obtained from full analyses of the temperature-dependent spectra of six-membered chelate complexes formed between 1,3-bis(methylseleno)-2,2-dimethylpropane (msdp) and chromium, molybdenum, and tungsten carbonyls.

RESULTS AND DISCUSSION

The new compound 1,3-bis(methylseleno)-2,2-dimethylpropane was chosen as a suitable ligand because in its n.m.r. spectrum each methylene proton is close-coupled only with its geminal partner. Couplings of these protons with the protons of methyl groups attached to the selenium and carbon atoms are over at least four bonds, and are unlikely to be resolved. When the ligand is complexed, the methylene protons can exist in equatorial or axial environments and their spectra below the coalescence temperature should consist of simple AB quartets, each component of which should be broadened by long-range couplings with the substituent methyl groups. The ligand was prepared by reacting sodium methyl selenide with 1,3-dibromo-2,2-dimethylpropane and was obtained as a vile-smelling, mobile, yellow liquid. The proton n.m.r. spectrum of the ligand exhibited signals of the expected relative intensities at τ 8·90 $[C(CH_3)_2]$, 7·97 ($Se{-}CH_3$), and 7·35 ($-Se{-}CH_2-$). These signals remained as singlets even below 200 K.

The complexes $[(msdp)M(CO)_4]$ were obtained in reasonable yields by displacement of the bidentate hydrocarbon ligand from bicyclo[2.2.1]heptadienetetracarbonylmetal complexes:



They were all obtained as yellow or orange crystalline materials soluble in chloroform and acetone, and molecular weight and molar conductance measurements in these solvents showed them to be neutral monomeric species.

TABLE 1

Molecular weights and molar conductances (in Me_2CO) for the complexes

Complex	M	Λ/Ω^{-1} cm^2
$[(msdp)Cr(CO)_4]$	408	0·1
$[(msdp)Mo(CO)_4]$	429	0·1
$[(msdp)W(CO)_4]$	657	0·2

N.M.R.—Spectra.—Temperature-dependent n.m.r. spectra (obtained at 90 MHz) showed that the complexes were stereochemically non-rigid. Above room temperature, the spectra of all the complexes were very similar and resembled that of the free ligand in consisting of three singlets. On cooling, coalescence phenomena became apparent, and all the spectra became effectively 'frozen out' below 240 K, there being no further changes in the spectra when $CFCl_3$ solutions of the complexes were cooled to 165 K. The full spectrum of $[(msdp)W(CO)_4]$ dissolved in $CDCl_3$ at 255 K is shown in Figure 1. The signal at τ 7·5 assigned to the protons of the ligand atom methyl groups, remained as a singlet at all temperatures examined. The signals in the region τ 8·7—8·9, assigned to the geminal methyl protons, consisted of a relatively broad singlet and a doublet of lesser intensity centred slightly further upfield. The signals in the region τ 6·7—7·5, assigned to the bridging methylene protons, quite clearly consisted of two AB quartets of unequal intensity, the parameters of which for each complex are recorded in Table 2. The coupling constants, J_{AB}, are of the order expected for geminal coupling constants and accordingly have been assigned negative values.[8] In every case, the relative intensities of the quartets corresponded exactly to those expected from the relative intensities of the geminal methyl proton signals. Line-shape fitting studies of the coalescence of the two AB quartets were performed using the DNMR2 program of Binsch and Kleier.[9] No assumptions were made in the calculations regarding the mechanism causing coalescence. Comparisons of experimental and simulated spectra for $[(msdp)Mo(CO)_4]$ at various temperatures and

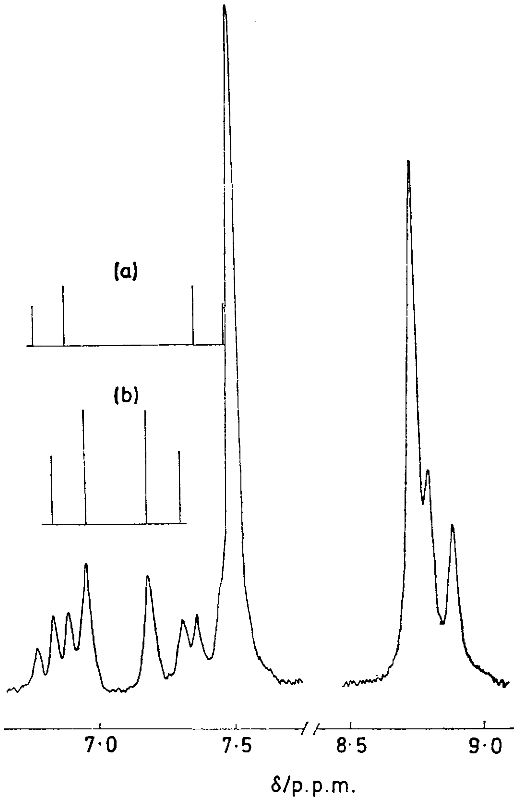


FIGURE 1 90 MHz ^1H n.m.r. spectra of $[(msdp)W(CO)_4]$ dissolved in $CDCl_3$ at 255 K: (a) methylene proton AB quartet I; (b) methylene proton AB quartet II

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[8] F. A. Bovey, 'Nuclear Magnetic Resonance Spectroscopy,' Academic Press, New York, 1969, p. 129.

[9] G. Binsch and D. A. Kleier, Program 140, Quantum Chemistry Program Exchange, Chemistry Department, Indiana University.

corresponding rate constants are illustrated in Figure 2. For each complex, good straight-line Arrhenius plots were obtained over the temperature range 240—330 K and thermodynamic parameters obtained from these plots are recorded in Table 3. Although the magnitudes of the estimated errors for the $\Delta S^{\ddagger}_{cc}$ values are such that it is possibly unwise to draw any conclusions concerning differences in this parameter between $[(msdp)Cr(CO)_4]$ and $[(msdp)Mo(CO)_4]$ and between $[(msdp)Mo(CO)_4]$ and $[(msdp)W(CO)_4]$, even allowing for maximum error, the change from a strongly negative value for $[(msdp)Cr(CO)_4]$ to a positive value for $[(msdp)W(CO)_4]$ is particularly striking.

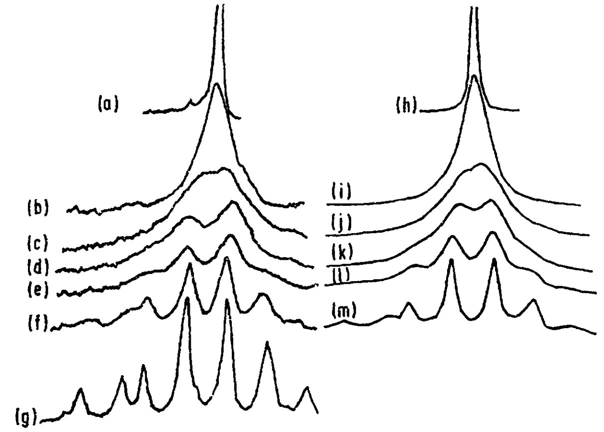

FIGURE 2 Comparison of experimental and simulated spectra for the bridging methylene protons of $[(msdp)Mo(CO)_4]$. T/K = (a) 310, (b) 280, (c) 270, (d) 265, (e) 260, (f) 250, (g) 230. $k_{I\rightarrow II}/s^{-1}$ = (h) 2140, (i) 257, (j) 112, (k) 76, (l) 45, (m) 18

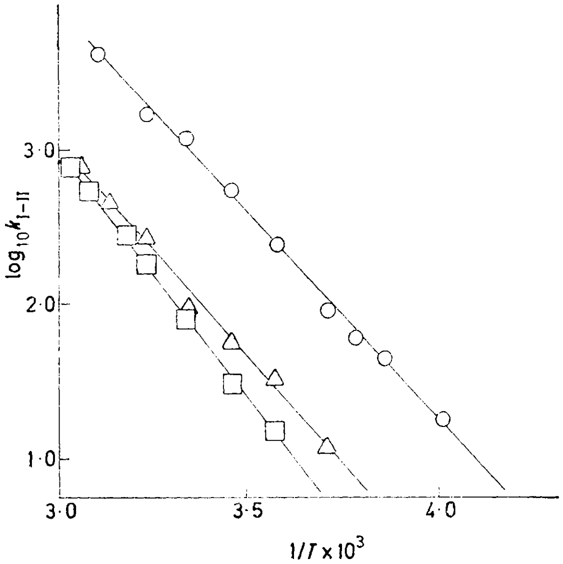

FIGURE 3 Arrhenius plots for the $[(msdp)M(CO)_4]$ complexes: M = △, Cr; ○, Mo; □, W

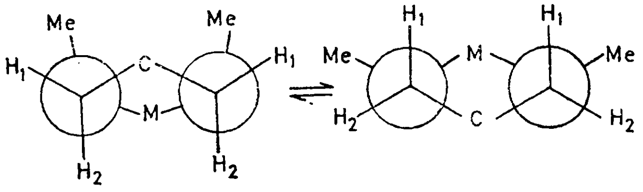

FIGURE 4 Interconversion of the two *syn*-configured, symmetric chair configurations

Whereas in five-membered ring systems, a number of conformers can have quite similar energies, it has been calculated that in octahedral systems, the symmetric chair conformation is highly favoured relative to the symmetric boat and various twist boat conformations.[2,3] Some confirmation of these predictions has come from recent experimental work by Cullen[10] who, using the '*R*-value' method of Lambert[11] and Buys[12,13] whereby the ring dihedral angle ψ for the $-CH_2-CH_2-$ fragments in six-membered rings may be calculated from the vicinal proton–proton coupling constants, has shown that the Group VI metal complexes of 1,3-bis(dimethylarsino)-2-t-butylpropane probably exist in a puckered symmetric chair conformation. A tetrahedral environment about a co-ordinated sulphur or selenium atom is now well-established[14,15] and the methyl substituents on the chelated ring possess

TABLE 2

90 MHz N.m.r. data for the complexes in $CDCl_3$

Complex	T/K	Methylene axial/equatorial proton AB quartet I			Methylene axial/equatorial proton AB quartet II		
		Population	$\Delta\nu_{AB}/Hz$	J_{AB}/Hz	Population	$\Delta\nu_{AB}/Hz$	J_{AB}/Hz
$[(msdp)Cr(CO)_4]$	240	0·46 ± 0·02	49·1 ± 0·5	−10·4 ± 0·2	0·54 ± 0·02	27·2 ± 0·5	−10·6 ± 0·2
$[(msdp)Mo(CO)_4]$	210	0·31 ± 0·02	47·8 ± 0·5	−11·0 ± 0·2	0·69 ± 0·02	19·4 ± 0·5	−11·0 ± 0·2
$[(msdp)W(CO)_4]$	250	0·40 ± 0·02	51·3 ± 0·5	−10·5 ± 0·2	0·60 ± 0·02	29·6 ± 0·5	−11·0 ± 0·2

TABLE 3

Thermodynamic parameters for the complexes: E_a, $\Delta G^{\ddagger}$, and $\Delta H^{\ddagger}$ in kJ mol^{-1}; $\Delta S^{\ddagger}$ in J K^{-1} mol^{-1}

Complex	$E_{a(I\rightarrow II)}$	$E_{a(II\rightarrow I)}$	$\Delta G^{\ddagger}_{300(I\rightarrow II)}$	$\Delta G^{\ddagger}_{300(II\rightarrow I)}$	$\Delta H^{\ddagger}_{300(I\rightarrow II)}$	$\Delta H^{\ddagger}_{300(II\rightarrow I)}$	$\Delta S^{\ddagger}_{cc(I\rightarrow II)}$	$\Delta S^{\ddagger}_{cc(II\rightarrow I)}$
$[(msdp)Cr(CO)_4]$	52·7 ± 3·5	53·1 ± 4·2	61·6 ± 0·5	61·5 ± 0·5	50·2 ± 4·2	50·6 ± 4·2	−38·0 ± 12·0	−36·0 ± 14·0
$[(msdp)Mo(CO)_4]$	51·7 ± 2·9	53·1 ± 5·0	55·9 ± 0·5	57·3 ± 0·5	49·3 ± 2·9	50·6 ± 5·0	−22·0 ± 14·0	−22·0 ± 14·0
$[(msdp)W(CO)_4]$	69·0 ± 3·5	69·4 ± 4·2	62·6 ± 0·5	63·2 ± 0·5	66·5 ± 3·5	66·9 ± 4·2	+13·0 ± 14·0	+12·0 ± 14·0

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[10] W. R. Cullen, L. D. Hall, J. T. Price, and G. Spendjian, *J. Amer. Chem. Soc.*, 1974, **96**, 410.

[11] J. B. Lambert, *Accounts Chem. Res.*, 1967, **4**, 87.

[12] H. R. Buys, *Rec. Trav. chim.*, 1969, **88**, 1003.

[13] H. R. Buys, *Rec. Trav. chim.*, 1970, **89**, 1253.

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

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

pseudo-axial or pseudo-equatorial character. Additionally, those attached to the selenium ligand atoms may be projected on the same side (*syn*-configuration) or on different sides (*anti*-configuration) of the ring. The *anti*-configuration has two equienergy, enantiomeric, and hence equally populated, symmetric chair conformations with one selenium-methyl group axial and the other equatorial. The *syn*-configuration has two symmetric chair conformations of different energy, one having both selenium-methyl groups equatorial and the other having them both axial.

We believe that the values for $\Delta S^{\ddagger}$ eliminate lone-pair inversion, and hence configurational interconversion, as the mechanism causing coalescence of the bridging methylene proton signals. Moreover, if the situation of slow configurational, combined with rapid conformational, change were to apply below the coalescence temperature, it is surprising that there were no further changes in the spectra down to 165 K as this would suggest that these very sterically crowded six-membered chelate ring systems were very much more flexible than cyclohexane.

We consider that the spectra can be interpreted only on the basis of the intraconversion of the two unequally populated, *syn*-configured, symmetric chair conformations as the unequal intensities of the signals of the geminal methyl protons rule out the presence of the analogous *anti*-configured conformations. That the lower-field signal for these protons consists of a broadened singlet suggests that increased non-bonding interactions between axial selenium-methyl groups causes some flattening of one of the chair conformations. This flattening would tend to displace the equatorial geminal methyl group from the MSe_2 plane, this reducing anisotropic effects and giving it a similar environment to its axial partner. Flattening of this chair conformation should even more markedly affect the signals arising from the bridging methylene protons and it can be seen from Table 2 that $\Delta\nu_{AB}$ was larger for one quartet than the other. The quartet with the smaller value of $\Delta\nu_{AB}$ corresponded in intensity to that expected from the intensity of the geminal methyl singlet. The bridging methylene groups are attached to centres of asymmetry arising from the tetrahedral environment about the selenium atoms and, in principle, an AB quartet should be expected for their signal even above coalescence. However, a small intrinsic non-equivalence would result in small values of $\Delta\nu/J$ and hence an apparent singlet.

The inversion process for the symmetric chair conformation of cyclohexane is generally believed to involve one of six possible twist-chair transition states. The statistics of the interconversion are consistent with a positive entropy of activation, of magnitude $R \ln 6$ as there are six degenerate pathways available for the process chair $\longrightarrow$ twist chair.[16] A similar process may be applicable for the inversion of the complexes of msdp, although here the two *syn*-configured symmetric chair conformations are not of equal energy. Therefore, on purely statistical grounds, a small positive entropy of activation might still be expected. However the strongly negative $\Delta S^{\ddagger}_{cc}$ value found for [(msdp)-$Cr(CO)_4$] implies that the transition state is more symmetrical and rigidly defined than the ground state, and suggests that for this complex it is not a twist-chair conformation. Bovey[17] has pointed out that only a transition *via* a planar form would give a negative value for $\Delta S^{\ddagger}_{cc}$ and a planar transition state for the chromium complex may well be imposed by severe non-bonding interactions between the ring substituents of a twist-chair conformation. It has been calculated that for cyclohexane a planar transition state is likely to lie at least 120 kJ mol^{-1} above the ground state and thus be inaccessible.[18] However, for [(msdp)$Cr(CO)_4$] it may be that steric strain in the ground state raises it to a higher energy level so that the $\Delta H^{\ddagger}$ involved in reaching a planar-like transition state is considerably less than that required for cyclohexane.

There should be a marked difference between the chromium–selenium and tungsten–selenium bond lengths and it is possible that the steric requirements for [(msdp)$W(CO)_4$] are relaxed somewhat, thus permitting a transition state approximating to a more normal twist-chair conformation.

The ΔH value for [(msdp)$Mo(CO)_4$] is slightly lower than that for [(msdp)$Cr(CO)_4$] and significantly lower than that for [(msdp)$W(CO)_4$], possibly because of increased M–Se multiple bonding in the case of the tungsten complex. The greater lability of [(msdp)$Mo(CO)_4$] might then be rationalised in terms of its reduced steric requirements compared with [(msdp)$Cr(CO)_4$] and of somewhat less M–Se multiple bonding compared with [(msdp)$W(CO)_4$].

EXPERIMENTAL

1,3-*Bis*(*methylseleno*)-2,2-*dimethylpropane*.—Dimethyl diselenide (9·4 g, 0·05 mol) was slowly treated with sodium (2·3 g, 0·10 g-atom) in liquid ammonia, at 195 K under dry nitrogen. To the solution so formed, 1,3-dibromo-2,2-dimethylpropane (10 g, 0·043 mol) was slowly added and the mixture stirred for 24 h. The ammonia was allowed to evaporate and 50 ml of dry ethanol was then added to the solid residue which was stirred for a further 3 days under dry nitrogen. The ethanol was distilled off and the residue extracted with chloroform. Removal of the chloroform gave 1,3-*bis*(*methylseleno*)-2,2-*dimethylpropane* contaminated with a small amount of 1,3-dibromo-2,2-dimethylpropane. No further purification of the material was attempted.

Interaction of 1,3-*Bis*(*methylseleno*)-2,2-*dimethylpropane with Bicyclo*[2.2.1]*heptadienetetracarbonylmetal*.—The requisite carbonyl complex (*ca*. 0·5 g) was heated under reflux for 30 min in n-heptane with a slight excess of 1,3-bis(methylseleno)-2,2-dimethylpropane. After cooling the solvent was evaporated off and the residue crystallised from chloroform–heptane to give crystals of 1,3-bis(methyl-

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[16] I. O. Sutherland, *Ann. Reports N.M.R. Spectroscopy*, 1971, **4**, 111.

[17] F. A. Bovey, F. P. Hood, E. W. Anderson, and R. L. Kornegay, *J. Chem. Phys.*, 1964, **41**, 2041.

[18] R. K. Harris, Ph.D. Thesis, Cambridge University, 1962, quoted by R. W. Murray, P. Story, and M. L. Kaplan, *J. Amer. Chem. Soc.*, 1966, **88**, 526.

seleno)-2,2-dimethylpropanetetracarbonylmetal (Found: C, 31·5; H, 3·9. Calc. for $C_{11}H_{16}CrO_4Se_2$: C, 31·3; H, 3·8. Found: C, 28·5; H, 3·4. Calc. for $C_{11}H_{16}MoO_4Se_2$: C, 28·3; H, 3·4. Found: C, 24·1; H, 3·1. Calc. for $C_{11}H_{16}WO_4Se_2$: C, 23·8; H, 2·9%).

N.m.r. Spectra.—These were obtained using a Bruker Hx 90 spectrometer. The line-shape fitting parameters were obtained using the DNMR2 program modified for use on the University of Dundee's ICI4130 computer.

We thank Mr. J. Low for assistance with the computing, the S.R.C. for a maintenance grant (to R.C.M.), and Mr. A. Chudek for obtaining the numerous n.m.r. spectra.

[4/1249 *Received, 24th June, 1974*]