Tin-119 Mössbauer Study of Complexes with Chlorine-bridged Tin–Molybdenum and Tin–Tungsten Bonds

By **William R. Cullen, Roland K. Pomeroy, John R. Sams,*** and **Tsang B. Tsin,** Department of Chemistry, University of British Columbia, Vancouver, Canada, V6T 1W5

Tin-119 Mössbauer spectra have been recorded for a number of complexes of the type $[L_2M(CO)_3(SnR_{3-n}Cl_n)Cl]$ (L_2 = αα′-bipyridyl, *o*-phenanthroline, dithiahexane; M = Mo or W; R = Me or Ph; n = 1—3), in which the M–Sn bond is bridged by a Cl atom. Measurements in applied magnetic fields of 50 kG show that the quadrupole coupling constant e^2qQ is positive and the asymmetry parameter η is small when n = 2 or 3. These facts, together with trends in isomer shift and quadrupole-splitting values, indicate that in these complexes W is a better σ-donor than Mo. For $[(bipy)Mo(CO)_3(SnPh_2Cl)Cl]$, $e^2qQ < 0$ and $\eta \simeq 0{\cdot}8$. It is concluded that the Mo atom and the two C atoms in this complex occupy approximately equatorial positions in the distorted trigonal bipyramidal Sn environment, and the large η is attributed to geometrical constraints imposed by the bridging Cl atom. The Mössbauer spectrum of $[(bipy)Mo(CO)_3(SnI_3)I]$ suggests partial dissociation of the complex to $[(bipy)Mo(CO)_3(I)I]$ and SnI_2.

IN 1968 Kummer and Graham[1] described the preparation of some seven-co-ordinate complexes containing Mo–Sn and W–Sn bonds. These complexes were obtained from reaction (1), where L_2 = αα-bipyridyl(bipy), *o*-phenanthroline(phen),[1a] or dithiahexane(dth),[1b] and M = Mo or W.

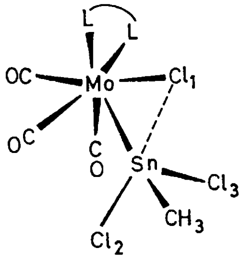
---

[1] (*a*) R. Kummer and W. A. G. Graham, *Inorg. Chem.*, 1968, **7**, 310; (*b*) R. Kummer and W. A. G. Graham, unpublished results.

Subsequent crystallographic studies[2,3] on [(bipy)Mo(CO)$_3$(SnMeCl$_2$)Cl] and [(dth)W(CO)$_3$(SnMeCl$_2$)Cl]

$$[\mathrm{L_2M(CO)_4}] + \mathrm{SnX_4} \longrightarrow [\mathrm{L_2M(CO)_3(SnX_3)X}] \quad (1)$$

showed the unique chlorine atom to be in close proximity to the tin atom as shown in the Figure. This close approach was taken to indicate a Sn–Cl bond, making the tin atom five-co-ordinate. This conclusion, however, should be treated with caution since the Sn–Cl distances of 2·805 and 2·96 Å, respectively, are much longer than 'normal' Sn–Cl bond lengths (*ca.* 2·38 Å). It is possible that the chlorine atom in question is forced into the neighbourhood of the tin atom by the crowded nature of the capped octahedral geometry about the transition-metal atom.



The structure of [(bipy)Mo(CO)$_3$(SnMeCl$_2$)Cl] as reported in ref. 2 (LL = bipy = $\alpha\alpha'$-bipyridyl). A similar structure was found for [(dth)W(CO)$_3$(SnMeCl$_2$)Cl] in ref. 3.

Therefore it was of interest to compare the Mössbauer spectra of these complexes with those of complexes containing a tin–transition-metal bond in which the tin atom does not have such a chlorine atom in its close environment. Herein we report details of such a study.

RESULTS AND DISCUSSION

We begin by considering in what ways the Mössbauer parameters of the present compounds might be expected to differ from those of other compounds with tin–transition-metal bonds but in which the tin atom is four-co-ordinate. The three most obvious factors to consider are (i) differences in σ-donor ability of the transition-metal atom, (ii) differences in M→Sn d_π–d_π bonding, and (iii) the presence of the bridging Cl in the Mo and W derivatives.

(i) The ^{119}Sn isomer shift is affected by changes in both 5*s* and 5*p* electron density, but is primarily sensitive to the former. An increase in *s* donor ability of a ligand will increase δ, whereas an increase in *p* donor strength will decrease δ by shielding the 5*s* electron density from the nucleus. Recently Bancroft *et al.*[4] have shown that the *s* character of the Sn–L bond increases in the order L = Cl < Ph < Me < Mn(CO)$_5$ < Fe(CO)$_2$(cp) (cp = π-C$_5$H$_5$). The magnitude of the quadrupole splitting, $|\Delta E_Q|$, depends on the asymmetry of the 5*p* orbital charge distribution at Sn and is therefore most sensitive to the *p* donor strength of the ligand. Since the quadrupole coupling constant e^2qQ is positive for both [Cl$_3$SnMn(CO)$_5$][5] and [Cl$_3$SnFe(CO)$_2$(cp)],[5,6] showing an excess of 5p_z electron density at Sn, it is clear that (at least in such four-co-ordinate species) an increase in *p* donor ability of the transition-metal moiety should lead to a larger $|\Delta E_Q|$.

(ii) Previous studies of compounds containing Sn–Fe and Sn–Mn bonds[6,7] have shown that these bonds are essentially pure σ_s in character. A very recent paper by Donaldson and co-workers[8] on complexes with Sn–Co bonds suggests that π bonding is of little or no importance in these derivatives as well. However, we should note that any π bonding between filled *nd* orbitals on the transition-metal atom and vacant 5*d* orbitals on tin would be expected to decrease δ *via* shielding effects. On the other hand, the m.o. calculations of Clark *et al.*[9] indicate that any π bonding involving the tin 5*d* orbitals would have no observable effect on ΔE_Q.

(iii) The influence of the bridging chlorine atom on the Mössbauer parameters is less easily predicted. In the series [X$_n$SnM$_{4-n}$] [X = Cl or Br; M = Mn(CO)$_5$ or Fe(CO)$_2$(cp)] it is found[6,10-12] that δ increases as *n* increases, despite the fact the X is much more electronegative than M. This indicates a very large 5*s* character in the Sn–M bonds and almost pure *p* character in the Sn–X bonds. If the situation is similar in the present compounds, then *p* electron withdrawal by the bridging chlorine should increase δ relative to compounds lacking such a bridging atom, although the effect is not likely to be large. The components of the electric-field gradient (e.f.g.) tensor might be more dramatically affected. The contribution to V_{zz} (the *z* component of the e.f.g.) of a point charge located a distance *r* from the nucleus is proportional to $\langle r^{-3}\rangle$, and in view of the long Sn–bridging-Cl distance this direct effect is probably small. Of more importance is the fact that the bond angles about Sn are significantly altered by the presence of the bridging Cl. This could have a pronounced effect on the asymmetry parameter η and might cause a re-orientation of the principal axes of the e.f.g. Thus, η and the sign of V_{zz} are likely to be much more sensitive than $|\Delta E_Q|$ to the presence of the bridging Cl.

SnCl$_3$ *Derivatives*.—It can be seen from Table 1 that both isomer shifts and quadrupole splittings for [(bipy)Mo(CO)$_3$(SnCl$_3$)Cl] and [(dth)Mo(CO)$_3$(SnCl$_3$)Cl] are substantially smaller than the corresponding values

---

[2] M. Elder and D. Hall, *Inorg. Chem.*, 1969, **8**, 1268.

[3] M. Elder and D. Hall, *Inorg. Chem.*, 1969, **8**, 1273.

[4] G. M. Bancroft, K. D. Butler, A. T. Rake, and B. Dale, *J.C.S. Dalton*, 1972, 2025.

[5] B. A. Goodman, R. Greatrex, and N. N. Greenwood, *J. Chem. Soc.* (*A*), 1971, 1868.

[6] S. R. A. Bird, J. D. Donaldson, A. F. LeC. Holding, B. J. Senior, and M. J. Tricker, *J. Chem. Soc.* (*A*), 1971, 1616.

[7] W. R. Cullen, J. R. Sams, and J. A. J. Thompson, *Inorg. Chem.*, 1971, **10**, 843.

[8] S. R. A. Bird, J. D. Donaldson, A. F. LeC. Holding, S. Cenini, and B. Ratcliff, *Inorg. Chim. Acta*, 1974, **8**, 149.

[9] M. G. Clark, A. G. Maddock, and R. H. Platt, *J.C.S. Dalton*, 1972, 281.

[10] D. E. Fenton and J. J. Zuckerman, *J. Amer. Chem. Soc.*, 1968, **90**, 6226; *Inorg. Chem.*, 1969, **8**, 1772.

[11] C. Wynter and L. Chandler, *Bull. Chem. Soc. Japan*, 1970, **43**, 2115.

[12] S. Onaka, Y. Sasaki, and H. Sano, *Bull. Chem. Soc. Japan*, 1971, **44**, 726.

for [(cp)Mo(CO)$_3$SnCl$_3$], which presumably contains a four-co-ordinate tin atom. Although some differences might be expected between the donor abilities of the L$_2$Mo(CO)$_3$Cl and (cp)Mo(CO)$_3$ moieties, it is very likely that the bridging Cl atom in the former complexes is responsible for at least part of the large differences in the Mössbauer parameters. We would anticipate the bridging Cl–Sn interaction to be maximized in compounds containing the SnCl$_3$ group since it is a stronger Lewis acid than SnRCl$_2$ or SnR$_2$Cl groups. This has been confirmed by the very recent structure determination of [(dth)Mo(CO)$_3$(SnCl$_3$)Cl].[13] The Sn–Cl (bridging) distance (2·78 Å) and Sn–Mo bond length (2·69 Å) are both slightly shorter than the corresponding values in the SnMeCl$_2$ case (2·805 and 2·753 Å, respectively). The bond angles about Sn are also closer to the regular trigonal bipyramidal values in the SnCl$_3$ complex.

For [(bipy)M(CO)$_3$(SnCl$_3$)Cl] (M = Mo or W), application of a 50 kG longitudinal magnetic field at 4·2 K revealed that in both cases $e^2qQ > 0$ and η was small, less than *ca.* 0·3. The positive coupling constants indicate an excess of $5p_z$ electron density at Sn, so that V_{zz} must lie essentially along the Sn–M direction. The small values of η are consistent with point-charge predictions[14,15] for trigonal bipyramidal SnAB$_4$ structures with A in an equatorial position.

The unusually low δ values for the two [L$_2$Mo(CO)$_3$(SnCl$_3$)Cl] compounds and [(dth)W(CO)$_3$(SnCl$_3$)Cl] are surprising since most other transition-metal derivatives containing the SnCl$_3$ group show $\delta > 1·6$ mm s^{-1}, and for [(cp)Mo(CO)$_3$SnCl$_3$], $\delta = 1·73$ mm s^{-1}. It should be noted (Table 1) that there is a regular decrease in δ as one goes from [Mn(CO)$_5$SnCl$_3$] to [Fe(CO)$_4$(Cl)SnCl$_3$] to [Co(CO)$_4$SnCl$_3$]. Bird *et al.*[8] have suggested that the smaller isomer shift in the Co(CO)$_4$ derivative is due to the greater electronegativity of the Co(CO)$_4$ group compared with that of the Mn(CO)$_5$ group. A similar argument is able to rationalize the Mössbauer data for the [L$_2$Mo(CO)$_3$Cl] and [(dth)W(CO)$_3$Cl] complexes, since a greater electronegativity of these groups would allow more *s* character in the Sn–Cl bonds which would lower δ, and at the same time decrease the *p*-orbital charge imbalance at tin, accounting for the smaller ΔE_Q. The addition of the fourth Sn–Cl bond in these complexes would then further reduce the isomer shift.

TABLE 1

Mössbauer parameters at 80 K for complexes containing the SnCl$_3$ group [a]

	δ/mm s^{-1} [b]	ΔE_Q/mm s^{-1} [c]	Ref.[d]
[(bipy)Mo(CO)$_3$(SnCl$_3$)Cl]	1·30	+1·29 [e]	
[(dth)Mo(CO)$_3$(SnCl$_3$)Cl]	1·41	1·32	
[(bipy)W(CO)$_3$(SnCl$_3$)Cl]	1·68	+1·67 [e]	
[(phen)W(CO)$_3$(SnCl$_3$)Cl]	1·66	1·66	
[(dth)W(CO)$_3$(SnCl$_3$)Cl]	1·45	1·48	
[Mn(CO)$_5$SnCl$_3$]	1·68	+1·57 [f]	12
[(cp)Fe(CO)$_2$SnCl$_3$]	1·77	+1·80 [f,g]	7
[Fe(CO)$_4$(SnCl$_3$)Cl]	1·55	1·40	19
cis-[Fe(CO)$_4$(SnCl$_3$)$_2$]	1·53	1·25	19
trans-[Fe(CO)$_4$(SnCl$_3$)$_2$]	1·53	1·26	19
[(C$_8$H$_{12}$)$_2$IrSnCl$_3$]	1·80	1·64	10
[Cl$_3$Ru$_2$(CO)$_5$SnCl$_3$]	1·71	+1·84 [e]	
[(cp)Mo(CO)$_3$SnCl$_3$]	1·73	1·73	

[a] bipy = αα-bipyridyl, phen = *o*-phenanthroline, dth = dithiahexane, cp = π-C$_5$H$_5$. [b] Isomer shift relative to BaSnO$_3$, ±0·03 mm s^{-1}. [c] Signs given refer to the sign of e^2qQ and for this work were determined with the sample in a longitudinal magnetic field of 50 kG. [d] This work unless otherwise noted. [e] $\eta \lesssim 0·03$. [f] Sign determined in ref. 5. [g] Sign determined in ref. 6.

The W derivatives with L$_2$ = bipy and phen have substantially larger δ and ΔE_Q values than does the dth compound, but the reason for this difference is not clear. In the case of [(cp)Fe(CO)$_2$SnCl$_3$], replacement of one carbonyl group by Ph$_3$P increases both δ and ΔE_Q for Sn by *ca.* 0·1 mm s^{-1},[7] showing that these parameters are quite sensitive to the nature of the other groups bonded to the transition-metal atom. However, we did not anticipate differences as great as those observed here, and it may be that there is a change in the bridging Cl–Sn interaction in these compounds.

The crystal structures of [(C$_8$H$_{12}$)$_2$IrSnCl$_3$],[16] [(cp)Fe(CO)$_2$SnCl$_3$],[17] and [Cl$_3$Ru$_2$(CO)$_5$SnCl$_3$][18] all reveal distorted tetrahedral geometries about the tin atoms, with M–Sn–Cl angles in the range 113—125° and Cl–Sn–Cl angles in the range 95—105°. The ^{119}Sn Mössbauer parameters in the ruthenium and iron complexes are almost identical, and in both cases e^2qQ is positive and $\eta \simeq 0$ as expected.

The results for [Fe(CO)$_4$(Cl)SnCl$_3$] and *cis*- and *trans*-[Fe(CO)$_4$(SnCl$_3$)$_2$] have been interpreted[19] as indicating the absence of any abnormal Sn–Cl interactions. In view of the present results we feel this conclusion should be treated with caution.

Organotin Chloride Derivatives.—Mössbauer data for the three groups of compounds studied in which there are either one or two tin–carbon bonds are given in Tables 2—4. Comparison of δ values for pairs of compounds in which only the Group VIB atom is changed reveals that δ appears to be marginally lower

TABLE 2

Mössbauer parameters at 80 K for complexes containing the SnMeCl$_2$ group [a]

Complex	δ/mm s^{-1}	ΔE_Q/mm s^{-1} [b]
[(bipy)Mo(CO)$_3$(SnMeCl$_2$)Cl]	1·54	+2·44 [c]
[(phen)Mo(CO)$_3$(SnMeCl$_2$)Cl]	1·54	2·53
[(dth)Mo(CO)$_3$(SnMeCl$_2$)Cl]	1·49	2·26
[(bipy)W(CO)$_3$(SnMeCl$_2$)Cl]	1·57	2·62
[(phen)W(CO)$_3$(SnMeCl$_2$)Cl]	1·61	2·64
[(dth)W(CO)$_3$(SnMeCl$_2$)Cl]	1·61	2·57
[Mn(CO)$_5$SnMeCl$_2$]	1·68	+2·62 [d]
[(cp)Mo(CO)$_3$SnMeCl$_2$]	1·68	2·83

[a] See Table 1 for ligand abbreviations. [b] See footnote *e* to Table 1. [c] $\eta \simeq 0·3$. [d] Ref. 4; $\eta = 0·46$.

---

[13] F. W. B. Einstein, personal communication.

[14] J. R. Sams, 'Magnetic Resonance **4**,' ed. C. A. McDowell, M.T.P. International Review of Science, 1972, University Park Press, Baltimore.

[15] G. M. Bancroft and R. H. Platt, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 59.

[16] P. Porta, H. M. Powell, R. J. Mawby, and L. M. Venanzi, *J. Chem. Soc.* (*A*), 1967, 455.

[17] P. T. Greene and R. F. Bryan, *J. Chem. Soc.* (*A*), 1970, 1696.

[18] M. Elder and D. Hall, *J. Chem. Soc.* (*A*), 1970, 245.

[19] N. Dominelli, E. Wood, P. Vasudev, and C. H. W. Jones, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 1077.

for the molybdenum complexes. In almost every case, however, the difference is no greater than the experimental uncertainty, so that there is really no significant difference in the *s* electron density at tin between corresponding tungsten and molybdenum derivatives.

TABLE 3

Mössbauer parameters at 80 K for complexes containing the SnPhCl$_2$ group [a]

	δ/mm s^{-1}	ΔE_Q/mm s^{-1} [b]
[(bipy)Mo(CO)$_3$(SnPhCl$_2$)Cl]	1·44	+2·10 [c]
[(phen)Mo(CO)$_3$(SnPhCl$_2$)Cl]	1·40	2·26
[(dth)Mo(CO)$_3$(SnPhCl$_2$)Cl]	1·50	2·20
[(bipy)W(CO)$_3$(SnPhCl$_2$)Cl]	1·48	2·21
[(phen)W(CO)$_3$(SnPhCl$_2$)Cl]	1·44	2·32
[(dth)W(CO)$_3$(SnPhCl$_2$)Cl]	1·55	+2·43 [d]
[Mn(CO)$_5$SnPhCl$_2$] [e]	1·63	2·52
[(cp)Fe(CO)$_2$SnPhCl$_2$] [e]	1·70	2·84

[a] See Table 1 for ligand abbreviations. [b] See footnote *c* to Table 1. [c] $\eta \simeq 0{\cdot}3$. [d] $\eta \simeq 0{\cdot}4$. [e] Ref. 4.

TABLE 4

Mössbauer parameters at 80 K for complexes containing the SnPh$_2$Cl group [a]

Complex	δ/mm s^{-1}	ΔE_Q/mm s^{-1} [b]
[(bipy)Mo(CO)$_3$(SnPh$_2$Cl)Cl]	1·47	−2·49 [c]
[(phen)Mo(CO)$_3$(SnPh$_2$Cl)Cl]	1·43	2·53
[(bipy)W(CO)$_3$(SnPh$_2$Cl)Cl]	1·48	2·50
[Mn(CO)$_5$SnPh$_2$Cl] [d]	1·63	2·52
[(cp)Fe(CO)$_2$SnPh$_2$Cl] [d]	1·58	2·54
[Co(CO)$_4$SnPh$_2$Cl] [e]	1·56	2·22

[a] See Table 1 for ligand abbreviations. [b] See footnote *c* to Table 1. [c] $\eta \simeq 0{\cdot}8$. [d] Ref. 4. [e] Ref. 12.

For both [(bipy)Mo(CO)$_3$(SnRCl$_2$)Cl] (R = Me or Ph), positive quadrupole coupling constants and small η values were found from magnetically perturbed Mössbauer spectra. Since the transition-metal moiety is more like an alkyl or aryl group than a halogen,[4] it is interesting to compare these results with those for diorganotin derivatives. Parish and Johnson [20] have shown that in such compounds a negative e^2qQ should only be observed if the C–Sn–C angle lies between the tetrahedral angle and its supplement, and as C–Sn–C increases from 109·5° η decreases from unity. Thus the positive e^2qQ and small η values observed here are fully consistent with the Mo–Sn–C angle of *ca.* 127° found [2] in [(bipy)Mo(CO)$_3$(SnMeCl$_2$)Cl].

The positive coupling constants observed in all the compounds containing SnCl$_3$, SnMeCl$_2$, and SnPhCl$_2$ groups for which the signs were determined, together with the fact that for a given L$_2$ the W derivative always gives a larger ΔE_Q than does the Mo complex, indicates that W is a better *p* electron donor towards Sn than is Mo. This would be expected to produce lower δ values in the W complexes (for a given L$_2$) by shielding, but as we have noted above this is not observed. This leads us to conclude that W must also be a slightly better *s* electron donor than Mo, and hence an overall better σ-donor in these compounds.

Another interesting feature of the positive e^2qQ for [(bipy)Mo(CO)$_3$(SnPhCl$_2$)Cl] is that it appears to confirm that the phenyl group occupies an analogous position to that of the methyl group in [(bipy)Mo(CO)$_3$(SnMeCl$_2$)Cl] (see Figure). This conclusion may be reached on the basis of partial quadrupole splitting (p.q.s.) calculations. Of course for structures as highly distorted as these, such calculations are not expected to provide ΔE_Q values in very close numerical agreement with measured values, but the predicted sign of e^2qQ should be quite reliable. To estimate an approximate p.q.s. value for the [(bipy)Mo(CO)$_3$] moiety, which for brevity we denote (p.q.s.)$_{\mathrm{Mo}}$, we have taken (p.q.s.)$_{\mathrm{Cl}}{}^{\mathrm{TBA}} = 0$ (TBA = trigonal bipyramidal apical), (p.q.s.)$_{\mathrm{Cl}}{}^{\mathrm{TBE}} = -0{\cdot}30$ (TBE = trigonal bipyramidal equatorial), and (p.q.s.)$_{\mathrm{Me}}{}^{\mathrm{TBE}} = -1{\cdot}10$ mm s^{-1}. These values have been found to give good agreement with observed quadrupole splittings for a wide range of five-co-ordinate organotin compounds.[21] These p.q.s. values, together with the observed [2] bond angles about tin in [(bipy)Mo(CO)$_3$(SnMeCl$_2$)Cl] and an assumed value for (p.q.s.)$_{\mathrm{Mo}}$, were read into a computer programme which diagonalizes the e.f.g. tensor and computes ΔE_Q and η values. Several different (p.q.s.)$_{\mathrm{Mo}}$ values were tried, and it was found that for (p.q.s.)$_{\mathrm{Mo}} = -0{\cdot}70$ mm s^{-1} the calculated parameters ($\Delta E_Q \simeq +2{\cdot}4$ mm s^{-1}, $\eta \simeq 0{\cdot}4$) were in satisfactory agreement with the measured quantities (Table 2). With this (p.q.s.)$_{\mathrm{Mo}}$ value * and (p.q.s.)$_{\mathrm{Ph}}{}^{\mathrm{TBE}} = -1{\cdot}00$ mm s^{-1},[21] the calculations were repeated for [(bipy)Mo(CO)$_3$(SnPhCl$_2$)Cl], with the Ph group assumed in turn to be in each of the three sites not occupied by the Mo and bridging Cl atoms, and with the bond angles taken from the corresponding methyltin compound.[2] Only when Ph was in the position occupied by Me in [(bipy)Mo(CO)$_3$(SnMeCl$_2$)Cl] was e^2qQ found to be positive, and the calculated values of $\Delta E_Q \simeq +2{\cdot}2$ mm s^{-1} and $\eta \simeq 0{\cdot}6$ are in reasonable agreement with the observed parameters.

A similar argument can be used to show that neither of the two Ph groups in the SnPh$_2$Cl derivatives occupies the site labelled Cl$_2$ in the Figure. Unless both Cl atoms are in apical positions, $|\Delta E_Q|$ is predicted to be substantially less in these compounds than in the corresponding monophenyltin complexes, contrary to what is observed (Tables 3 and 4). This conclusion is obtained whether one assumes the bond angles above or uses strict trigonal bipyramidal geometry.[14] The proposed structure is in agreement with Bent's conclusions [23] that the more electropositive groups should occupy equatorial positions in a trigonal bipyramidal arrangement. The negative e^2qQ found for [(bipy)Mo(CO)$_3$(SnPh$_2$Cl)Cl] is as expected for such a structure, and indicates that V_{zz} lies in direction roughly perpendicular to the plane of the Mo and two C atoms. The large η observed here is in contrast to the small η values (less than *ca.* 0·4) predicted for [MSnR$_2$X] derivatives [M = Mn(CO)$_5$ or Fe(CO)$_2$(cp); R = Me or Ph; X = Cl or Br],[4]

---

* This value is entirely reasonable in comparison with p.q.s. values derived for other transition-metal moieties bonded to tin.[4,22]

[20] R. V. Parish and C. E. Johnson, *J. Chem. Soc.* (*A*), 1971, 906.

[21] J. N. R. Ruddick, personal communication.

[22] G. M. Bancroft and K. D. Butler, *J.C.S. Dalton*, 1973, 1694.

[23] H. A. Bent, *Chem. Rev.*, 1961, **61**, 275.

and the measured[4] value of 0·35 in $[\mathrm{Me_2ClSnMn(CO)_5}]$. This is almost certainly a consequence of the geometrical constraints imposed by the bridging Cl atom in the present case.

$[\mathrm{(bipy)Mo(CO)_3(SnI_3)I}]$.—In this complex Kummer and Graham[1] observed more than the expected three CO stretching bands in the i.r. spectrum, which they ascribed to the presence of isomers. The Mössbauer spectrum consisted of three lines of approximately equal intensity, located at 1·28, 2·36, and 4·01 mm s^{-1} relative to $\mathrm{Ba^{119}SnO_3}$. This spectrum is best interpreted as showing the presence of two tin species, the two lower-velocity lines arising from a $\mathrm{Sn^{IV}}$ species with $\delta = 1{\cdot}82$ mm s^{-1} and $|\Delta E_Q| = 1{\cdot}08$ mm s^{-1}, and the high-velocity line from a $\mathrm{Sn^{II}}$ species with $\delta = 4{\cdot}01$ mm s^{-1} and $\Delta E_Q \simeq 0$. Since $\mathrm{SnI_2}$ is reported[24] to show no quadrupole splitting and an isomer shift of 3·85 mm s^{-1}, it seems likely that this complex is in fact partly dissociated according to:

$$[\mathrm{(bipy)Mo(CO)_3(SnI_3)I}] \rightleftharpoons [\mathrm{(bipy)Mo(CO)_3(I)I}] + \mathrm{SnI_2}$$

Similar processes have been observed previously.[25,26] In the CO stretching region an i.r. spectrum of $[\mathrm{(bipy)W(CO)_3(SnI_3)I}]$ prepared by the method of Kummer and Graham,[1] was almost identical with that of an authentic sample of $[\mathrm{(bipy)W(CO)_3(I)I}]$.[27]

TABLE 5

Analytical data (%) and carbonyl stretching frequencies for new complexes

Complex	Analytical data: Found (Calc.) C	H	N	ν(CO)(cyclohexane)/cm^{-1}
$[\mathrm{(phen)Mo(CO)_3(SnPhCl_2)Cl}]$	37·8 (38·08)	2·1 (1·99)	4·1 (4·23)	2011s, 1926m, 1903s
$[\mathrm{(phen)W(CO)_3(SnCl_3)Cl}]$	25·3 (25·43)	1·1 (1·13)	3·9 (3·94)	2027s, 1937sh, 1921s, b
$[\mathrm{(phen)W(CO)_3(SnPhCl_2)Cl}]$	32·7 (33·62)	1·9 (1·75)	3·55 (3·73)	2003s, 1903s, b
$[\mathrm{(dth)W(CO)_3(SnPhCl_2)Cl}]$	22·45 (22·55)	2·35 (2·18)		2007s, 1919s, b

EXPERIMENTAL

All compounds of the type $[\mathrm{L_2M(CO)_3(SnR_{3-n}Cl_n)Cl}]$ were prepared using essentially the method of Kummer and Graham.[1] However, in some cases dichloromethane was used as solvent in preference to acetone, since side reactions in the latter solvent appeared to be catalysed by trace amounts of water. Data for some derivatives not prepared by Kummer and Graham[1] are given in Table 5. The ruthenium complex $[\mathrm{Cl_3Ru_2(CO)_5SnCl_3}]$ was also prepared by the original method.[26,28]

^{119}Sn Mössbauer spectra were recorded with the samples at *ca.* 80 K in transmission geometry as previously described.[29] The velocity scale was calibrated using a ^{57}Co(Cu) source and iron-foil absorber, and isomer shifts are quoted relative to the $\mathrm{Ba^{119m}SnO_3}$ source. The data were least-squares fitted to Lorentzian components and no constraints were placed on the fitting parameters. The equipment and procedures employed in the magnetic-perturbation Mössbauer experiments have been published.[30] In every case reported here longitudinal fields of 50 kG were applied to the samples. N.m.r. spectra were obtained using a Varian T60 instrument and chemical shifts are given in p.p.m. downfield from internal $\mathrm{Me_4Si}$.

Preparation of $[\mathrm{(cp)Mo(CO)_3SnMeCl_2}]$. A solution of $[\{\mathrm{(cp)Mo(CO)_3}\}_2]$ (0·81 g, 2 mmol) in tetrahydrofuran (50 ml) was stirred over 1% sodium amalgam for 0·5 h to give $[\mathrm{(cp)Mo(CO)_3}]^-$.[31] The amalgam was then removed, $\mathrm{MeSnCl_3}$ (1·0 g, 4·2 mmol) in 50 ml tetrahydrofuran added, and the whole stirred at 40 °C for 1 h. The solvent was removed and the residue washed with cold light petroleum to remove $\mathrm{MeSnCl_3}$. The residue was extracted with three 50-ml portions of boiling heptane, and the extractions were filtered whilst hot. During filtration orange crystals of presumably $[\{\mathrm{(cp)Mo(CO)_3}\}_2\mathrm{SnMeCl}]$ separated. The heptane extractions were then cooled whereupon $[\mathrm{(cp)Mo(CO)_3SnMeCl_2}]$ in the form of a yellow powder was obtained. As a final purification the product was sublimed at 110 °C (0·2 mmHg) to give the pure *compound* (0·7 g, 43%), m.p. 120—121° (Found: C, 23·95; H, 1·95. $\mathrm{C_9H_8Cl_2MoO_3Sn}$ requires C, 24·04; H, 1·79); ν(CO) (cyclohexane) * 2029s, 1975w, 1967m, and 1841s cm^{-1} (lit.,[33] 2038, 1970, and 1841 cm^{-1}); ^{1}H n.m.r. resonances δ ($\mathrm{CDCl_3}$) 1·27 and 5·60 p.p.m., area ratio 3 : 5 (lit.,[33] 1·2 and 5·4 p.p.m.).

Preparation of $[\mathrm{(cp)Mo(CO)_3SnCl_3}]$. To a tetrahydrofuran solution of $[\mathrm{(cp)Mo(CO)_3}]^-$ prepared as described above was added an equimolar quantity of $\mathrm{Ph_3SnCl}$ and the resulting solution stirred for 2 h. The tetrahydrofuran was removed to leave $[\mathrm{(cp)Mo(CO)_3SnPh_3}]$, whose i.r. spectrum in the carbonyl region agreed well with that reported in the literature.[34] The $[\mathrm{(cp)Mo(CO)_3SnPh_3}]$ was dissolved in benzene and HCl gas was slowly bubbled through the stirred solution for 1 h. At this stage the i.r. spectrum of the reaction mixture showed carbonyl stretching bands associated with the product only. The solution was filtered and heptane added. Solvent was slowly removed using a water aspirator until crystallisation commenced. The solution was then cooled to afford a good yield of the *product* $[\mathrm{(cp)Mo(CO)_3SnCl_3}]$ in the form of yellow crystals, m.p. 170—172° (lit.,[35] 164°) (Found:

---

* Conformational isomers are expected for this complex, leading to the observation of more than the expected number of ν(CO) bands.[32]

[24] J. D. Donaldson and B. J. Senior, *J. Chem. Soc.* (*A*), 1969, 2358.

[25] A. J. Oliver and W. A. G. Graham, *Inorg. Chem.*, 1971, **10**, 1.

[26] R. K. Pomeroy, M. Elder, D. Hall, and W. A. G. Graham, *Chem. Comm.*, 1969, 381.

[27] M. H. B. Stiddard, *J. Chem. Soc.*, 1962, 4712.

[28] R. K. Pomeroy, Ph.D. Thesis, University of Alberta, 1972.

[29] P. A. Yeats, B. L. Poh, B. F. E. Ford, J. R. Sams, and F. Aubke, *J. Chem. Soc.* (*A*), 1970, 2188.

[30] J. N. R. Ruddick and J. R. Sams, *J.C.S. Dalton*, 1974, 470.

[31] R. G. Hayter, *Inorg. Chem.*, 1963, **2**, 1031.

[32] W. Jetz and W. A. G. Graham, *J. Amer. Chem. Soc.*, 1969, **91**, 3375.

[33] R. E. J. Bichler, H. C. Clark, B. K. Hunter, and A. T. Rake, *J. Organometallic Chem.*, 1974, **69**, 367.

[34] H. R. H. Patil and W. A. G. Graham, *Inorg. Chem.*, 1966, **5**, 1401.

[35] F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 1964, 179.

C, 20·4; H, 1·0. $C_8H_5Cl_3MoO_3Sn$ requires C, 20·44; H, 1·01); ν(CO) (cyclohexane) 2043s, 1986m, and 1971s cm^{-1}; ^1H n.m.r. resonance δ 5·72 p.p.m.

We thank Dr. W. A. G. Graham for information concerning the preparation of the dithiahexane derivatives prior to publication. We are grateful to Dr. F. W. B. Einstein for sending us the unpublished results of his crystal-structure determination. We also thank the National Research Council of Canada for financial support.

[4/2109 *Received*, 14*th October*, 1974]