J. Chem. Soc. (A), 1971

Preparation and Infrared Spectra of Some Group IV Metal-Tricarbonylnitrosyliron Derivatives

By M. Casey and A. R. Manning,* Department of Chemistry, University College, Belfield, Dublin 4, Ireland

Various complexes of the types $[(R_3M)Fe(CO)_2(NO)L]$. $[R = Ph, Me, Et, Bu^n, Cl, or Br; M = Ge, Sn, or Pb;$ $L = CO, Ph_3P, (PhO)_3P, or PhEt_2As]$ and $[(Ph_2M){Fe(CO)_2(NO)L}_2]$ [M = Sn or Pb; L = CO, (PhO)_3P, or PhEt₂As] are described, and a new method of preparing compounds containing transition metal to tin bonds is reported. On the basis of their i.r. spectra, it is suggested that these compounds have trigonal bipyramidal coordination about the iron atom, and a linear M-Fe-L system. When R_aM is Ph₂CISn or PhCl₂Sn, or L is PhEt₂As isomerism is observed owing to restricted rotation about the Fe-Sn or Fe-As bond. In solution in acetonitrile $[(Ph_{3}M)Fe(CO)_{3}(NO)]$ and $[(Ph_{2}M){Fe(CO)_{3}(NO)}_{2}]$ (M = Sn or Pb) dissociate completely, and reversibly to give the $[Fe(CO)_3(NO)]^-$ ion.

ALTHOUGH there have been many preparative and structural studies of compounds containing a Group IV metal bonded to a cobalt carbonyl moiety,¹⁻²¹ the only reported work on their isoelectronic analogues, which contain the Fe(CO)₃NO and related groups, is the preparation of $[(ClSn){Fe(CO)_2(NO)L}_3]$ and $[(Sn{Fe(CO)_2^-})^2]$ $(NO)L_{4}$ [L = CO, Ph₃P, (C₆H₁₁)₃P, or Ph₃As].^{22,23}

We report here the preparation and i.r. spectra of compounds in which germanium(IV), tin(IV), or lead(IV) is bonded to one or two $Fe(CO)_2(NO)L$ moieties [L =CO, Ph₃P, (PhO)₃P, or PhEt₂As]. We also report a new route for the preparation of compounds containing one tin-transition-metal bond. Those complexes which contain a Ph₂ClSn or PhCl₂Sn group, or a PhEt₂As ligand exhibit isomerism in solution owing to restricted rotation about the Fe-Sn or Fe-As bond. In acetonitrile solution, the Cl₃M and Br₃Sn derivatives decompose, but those of the type [Ph₃MFe(CO)₃(NO)] or [(Ph₂M)- ${\rm Fe(CO)_3(NO)}_2$ (M = Sn or Pb) dissociate completely and reversibly to the $[Fe(CO)_3NO]^-$ ion. When Ph_3P or PhEt₂As is co-ordinated to the iron atoms, this dissociation does not take place.

EXPERIMENTAL

256

Chemicals were commercial grade and were used without further purification. The preparation of the mercury complexes $[Hg{Fe(CO)_2(NO)L}_2]$ $[L = CO, Ph_3P, (PhO)_3P,$ or PhEt₂As] has been described elsewhere 22-25 All reactions were carried out in dried and deoxygenated solvents under nitrogen and at room temperature unless stated otherwise.

- ¹ J. G. A. Luitjen, Organometallic Chem. Rev., 1969, 5B, 693. ² F. Hein, P. Kleinert, and W. Jehn, Naturwiss., 1957, 44,
- 34.³ W. Hieber and R. Breu, Chem. Ber., 1957, 90, 1270.
- ⁴ F. Hein and W. Jehn, Annalen, 1965, 684, 4.
- ⁵ D. J. Patmore and W. A. G. Graham, Inorg. Chem., 1966, **5**, 1045.
- ⁶ D. J. Patmore and W. A. G. Graham, Inorg. Chem., 1966, **5**, 2222.
- 7 D. J. Patmore and W. A. G. Graham, Inorg. Chem., 1967, 6, 981.
- ⁸ D. J. Patmore and W. A. G. Graham, Inorg. Chem., 1968, 7, 771.
- ⁹ S. A. Fieldhouse, B. H. Freeland, and R. J. O'Brien, Chem. Comm., 1969, 1297.
- ¹⁰ K. M. Mackay and R. D. George, Inorg. Nuclear Chem. Letters, 1970, 6, 289.
- ¹¹ A. P. Hagen and A. G. MacDiarmid, Inorg. Chem., 1967, 6, 686. ¹² E. B. Fleischer and P. A. Tasker, Inorg. Nuclear Chem.
- Letters, 1970, 6, 345.

Salts of the $[Fe(CO)_2(NO)L]^-$ anions were best prepared by shaking solutions of the mercury derivatives $[Hg{Fe(CO)_2(NO)L}_2]$ (ca. 1–2 g) in tetrahydrofuran (50 ml) with 1% sodium amalgam.

Complexes containing germanium, tin, or lead bonded to iron were prepared by two routes. (i) This was by the reaction of the $\{Fe(CO)_2(NO)L\}^-$ salts with (a) GeCl₄, $R_3SnCl (R = Et, Buⁿ, or Ph), Me_3PbOAc, and Ph_3PbCl$ to give the $[(R_3M)Fe(CO)_2(NO)L]$ derivatives, and (b) Ph₂SnCl₂ and Ph₂PbCl₂ to give [(Ph₂Sn){Fe(CO)₂(NO)L}₂] and [(Ph₂Pb){Fe(CO)₂(NO)L}₂]. Equimolar quantities of the reactants were used for the first group of reactions, and for the second mole ratios for $[Fe(CO)_2(NO)L]^-$ to Ph_2MCl_2 of 2:1. At the completion of the reaction, the products were isolated by removal of the solvent at reduced pressure, purified by chromatography (benzene-alumina), and recrystallized from pentane. Yields were ca. 50% {except [(Cl_3Ge)(Fe(CO)₃(NO)], 25%}.

(ii) The method used for complexes containing one Fe-Sn bond, was the direct reaction of a solution or suspension of the mercury derivatives [Hg{Fe(CO)₂(NO)L}₂] (ca. 1 g) $[L = CO, Ph_3P, or (PhO)_3P]$ with a tin(rv) halide (reactant mole ratio 1:2). The tetrahalides $SnCl_4$ and SnBr₄ reacted rapidly at room temperature in benzene. More vigorous conditions were required for the reaction of $[Hg{Fe(CO)_3NO}_2]$ with PhSnCl₃ and Ph₂SnCl₂ (under reflux in benzene), and Ph₃SnCl (under reflux in tetrahydrofuran). These reactions were not always complete, and often gave $[ClHgFe(CO)_3(NO)]$ as a byproduct. At the completion of the reaction the precipitated solids were removed by filtration before isolation of the desired products

- ¹³ D. D. Spencer, J. L. Kirsch, and T. L. Brown, Inorg. Chem., 1970, 9, 235.
- ¹⁴ J. D. Graybeal, S. D. Ing, and M. W. Hsu, Inorg. Chem., 1970, **9**, 678.
- J. K. Stalick and J. A. Ibers, J. Organometallic Chem., 1970, **22**, 213. ¹⁶ K. Emerson, P. R. Ireland, and W. T. Robinson, Inorg.
- Chem., 1970, 9, 436. ¹⁷ T. L. Brown, P. A. Edwards, C. B. Harris, and J. L. Kirsch,
- Inorg. Chem., 1969, 8, 763. ¹⁸ K. L. Watters, J. N. Brittain, and W. M. Risen, jun., Inorg. Chem., 1969, 8, 1347. A. G. Robiette, G. M. Sheldrick, R. N. F. Simpson, B. J.
- Aylett, and J. A. Campbell, J. Organometallic Chem., 1968, 14, 279.
- 20 O. Kahn and M. Bigorgne, J. Organometallic Chem., 1967, 10, 137.
 ²¹ W. T. Robinson and J. A. Ibers, *Inorg. Chem.*, 1967, 6, 1208.
 ²² W. Hieber and H. Beutner, *Z. anorg. Chem.*, 1963, 320, 101.
 ²³ W. Hieber and W. Klingshirn, *Z. anorg. Chem.*, 1963, 323,
- 292.
 - ²⁴ R. B. King, Inorg. Chem., 1963, 2, 1275.
 - ²⁵ M. Casey and A. R. Manning, J. Chem. Soc. (A), 1970, 2258.

which were purified by recrystallization from pentane or benzene-hexane. Reaction yields were ca. 50-80% (except in tetrahydrofuran, ca. 12%).

The complex $[(Ph_3Sn)Fe(CO)_2(NO)(PPh_3)]$ was prepared by the reaction of $[(Ph_3Sn)Fe(CO)_3(NO)]$ and Ph_3P (mole ratio 1:1) in benzene solution under the influence of u.v. lying between 1700 and 2150 cm^{-1} are summarised in Tables 2 and 3.

RESULTS AND DISCUSSION

All the compounds described are yellow to red crystalline solids, except $[(Bu_{3}Sn)Fe(CO)_{3}(NO)]$ and

TABLE 1

M.p. and analytical data for the complexes described

			Found (%)				Reqd. (%)			
Compound	Formula	M.p. "	C	н	N	Hal. d	C	н	N	Hal.
$[(Ph_3Sn)Fe(CO)_3(NO)]$	C ₉₁ H ₁₅ FeNO ₄ Sn	122° b	48.2	$3 \cdot 1$	2.7		48.4	$2 \cdot 9$	2.7	
[(Ph ₂ ClŚn)Fe(ĆŎ) ₂ (NŐ)]	C ₁₅ H ₁₀ ClFeNO ₄ Sn	67	37.9	$2 \cdot 4$	$2 \cdot 4$		37.7	$2 \cdot 1$	$2 \cdot 9$	$7 \cdot 4$
[(PhCl ₂ Sn)Fe(CO) ₃ (NO)]	C₄H₅Ĉl₂FeNO₄Ŝn	76	25.0	$1 \cdot 1$	3.1	16.7	$24 \cdot 8$	$1 \cdot 2$	$3 \cdot 2$	16.3
$[(Cl_{3}Sn)Fe(CO)_{3}(NO)]$	C ₃ Cl ₃ FeNO ₄ Sn	ء 101	9.3		$3 \cdot 4$	26.5	9.1		3.6	26.9
$[(Br_sSn)Fe(CO)_s(NO)]$	C ₃ Br ₃ FeNO ₄ Sn	85 °	6.4		$2 \cdot 4$	45.2	6.8		2.7	45.4
(Ph ₃ Pb)Fe(CO) ₃ (NO)	C ₂₁ H ₁₅ FeNO ₄ Pb	90 ^b	41.8	$2 \cdot 5$	$2 \cdot 3$		41.5	$2 \cdot 5$	$2 \cdot 3$	
(Me _a Pb)Fe(CO) _a (NO)	C,H,FeNO,Pb	91 - 92	17.3	$2 \cdot 6$	3.0		17.1	$2 \cdot 2$	3.3	
(Cl _a Ge)Fe(CO) _a (NO)	C ₃ Cl ₃ FeGeNO ₄	71 ^b	10.3		3.6		10.3		$4 \cdot 0$	
[(Ph ₃ Sn)Fe(CO) ₂ (NO)(PPh ₃)]	C ₃₈ H ₃₀ FeNO ₃ PSn	179 b	60.4	$4 \cdot 0$	1.8		60.5	4 ·0	1.9	
(Ph ₃ Sn)Fe(CO), (NO)(AsEt, Ph)]	C ₃₀ H ₃₀ AsFeNO ₃ Sn	106 °	50.9	4.4	1.8		51.2	4.3	$2 \cdot 0$	
(Cl,Sn)Fe(CO),(NO)(PPh,)	C ₂₀ H ₁₅ Cl ₂ FeNO ₃ PSn	ء 145	38.0	$2 \cdot 4$	1.9	17.3	38.2	$2 \cdot 4$	$2 \cdot 2$	16.9
$[(Br_3Sn)Fe(CO),(NO)(PPh_3)]$	C ₂₀ H ₁₅ Br ₃ FeNO ₃ PSn	ه 130	31.5	1.9	1.8		31.5	$2 \cdot 0$	1.9	31.4
$[(Cl_{a}Sn)Fe(CO)_{a}(NO){P(OPh)_{a}}]$	C ₂₀ H ₁₅ Cl ₃ FeNO ₆ PSn	102	$35 \cdot 1$	1.4	1.8	15.7	$35 \cdot 4$	$2 \cdot 2$	$2 \cdot 1$	15.7
$[(Ph_2Sn){Fe(CO)_3(NO)}_2]$	$C_{18}H_{10}Fe_{2}N_{2}O_{8}Sn$	129 5	35.0	1.7	4.2		$35 \cdot 4$	1.7	4.6	
$[(Ph_2Pb)]$ Fe $(CO)_3(NO)]_2$	C ₁₈ H ₁₀ Fe ₂ N ₂ O ₈ Pb	81 8	30.8	1.5	3.9		30.9	1.4	4 ·0	
$[(Ph_3Sn)]$ $Fe(CO)_2(NO)[P(OPh)_3]$	$C_{52}H_{40}Fe_2N_2O_{12}P_2Sn$	122 - 124	$52 \cdot 6$	$3 \cdot 4$	$2 \cdot 3$		$53 \cdot 1$	$3 \cdot 4$	$2 \cdot 4$	
$[(Ph_2Sn)]$ Fe(CO) ₂ (NO)(AsEt ₂ Ph)] ₂]	C ₃₆ H ₄₀ As ₂ Fe ₂ N ₂ O ₆ Sn	9495	44 ·0	4 ·1	$2 \cdot 5$		44.3	4.1	$2 \cdot 9$	
$[(Ph_2Pb)]$ $Fe(CO)_2(NO)(AsEt_2Ph))$	$C_{36}H_{40}As_2Fe_2N_2O_6Pb$	8990	40·6	3.9	$2 \cdot 5$		40.6	3 ∙8	$2 \cdot 6$	
^a Determined in sealed tube	es. ^b Decomposed witho	out melting.	۰ Melte	d with	decor	npositio	n. a (Cl or l	Br.	

TABLE 2

The i.r. spectra of $[(R_3M)Fe(CO)_2(NO)L]$ derivatives between 1700 and 2150 cm⁻¹ for heptane solutions unless otherwise stated; peak positions (cm⁻¹) with relative peak heights in parentheses

Absorption bands ^a							
v(CO)	$\nu(NO)$						
2065 (10), 2010 (5.0), 1980 (9.2)	1773 (5.6)						
2056 (9.6), 1997 (5.6), 1965 (10)	1760 (5.0)						
2056 (8.1), 1998 (5.3), 1967 (10)	1760 (4 ·7)						
2076 (10), 2026sh, 2023 (3·9), 2001 (5·1), 1987 (5·4)	1794 (5·1), 1776 (2·1)						
2085 (10), 2041 (4·7), 2035sh, 2010 (6·9), 2003sh	1817 (4.5), 1800 (4.4)						
2101 (10), 2058 (4.4), 2032 (8.1)	1825 (6.4)						
2098 (10), 2054 (4.1), 2028 (8.5)	1820 (6.6)						
2060 (10), 2006 (3.6), 1978 (7.0)	1768 (4.4)						
$2054(10), 1995(5\cdot2), 1965(10)$	1755 (5 ·7)						
2103(7.9), 2059(5.1), 2035(10)	1826 (7.4)						
1988 (3.3), 1928 (10)	1732 (5.8)						
1984sh, 1982 (3·1), 1925sh, 1922 (10)	1734sh, 1726 (5·3)						
2033 (3.5), 1980 (10)	1781 (7.0)						
2047 (3.9), 1997 (10)	1797 (7.9)						
2027 (3.5), 1976 (10)	1777 (7·1)						
	Absorption bands * ν (CO) 2065 (10), 2010 (5·0), 1980 (9·2) 2056 (9·6), 1997 (5·6), 1965 (10) 2056 (8·1), 1998 (5·3), 1967 (10) 2076 (10), 2026sh, 2023 (3·9), 2001 (5·1), 1987 (5·4) 2085 (10), 2041 (4·7), 2035sh, 2010 (6·9), 2003sh 2101 (10), 2058 (4·4), 2032 (8·1) 2098 (10), 2054 (4·1), 2028 (8·5) 2060 (10), 2006 (3·6), 1978 (7·0) 2054 (10), 1995 (5·2), 1965 (10) 2103 (7·9), 2059 (5·1), 2035 (10) 1988 (3·3), 1928 (10) 1984 (3·5), 1980 (10) 2047 (3·9), 1997 (10) 2027 (3·5), 1976 (10)						

sh = Shoulder. ^a Carbon disulphide solution.

irradiation (Philips HPR 125 w lamp) for 4 h. The reaction mixture was then chromatographed (silica gelbenzene) to give the required product (30%). Significant amounts of [(Ph₃P)₂Fe(CO)₃]²⁶ and [(Ph₃P)₂Fe(NO)₂]²⁷ were also formed.

Melting point and analytical data for these compounds are summarised in Table 1.

I.r. spectra were obtained as described previously; ²⁵ the frequencies and relative intensities of the absorption bands

²⁶ A. F. Clifford and A. K. Mukhergee, *Inorg. Chem.*, 1963, 2, 151.

 $[(Et_3Sn)Fe(CO)_3(NO)]$ which are red oils. They are soluble in organic solvents. All are more or less unstable; those containing the GeCl₃, SnCl₃, SnBr₃, and SnCl₂Ph groups decompose slowly even at -20° under nitrogen. The replacement of a carbonyl group by a tertiary phosphine, phosphite, or arsine ligand brings about an increase in compound stability. Spectroscopic studies show that in solution the decomposition products

²⁷ D. E. Morris and F. Basolo, J. Amer. Chem. Soc., 1968, **90**, 2531.

TABLE 3

The i.r. spectra of $[(Ph_2M){Fe(CO)_2(NO)L}_2]$ complexes between 1700 and 2100 cm⁻¹ for heptane solutions unless otherwise stated; peak positions (cm⁻¹) with relative peak heights in parentheses

	Absorption bands				
Compound	ν (CO) Vibrations	ν (NO) Vibrations			
$[(\mathrm{Ph}_2\mathrm{Sn})\{\mathrm{Fe}(\mathrm{CO})_3\mathrm{NO}\}_2]$	2074 (3·4), 2060 (10), 2021 (2·7), 2017 (2·7), 1995sh 1993 (5·1) 1989sh	1798 (1.8), 1787sh, 1778 (2.7),			
$[(Ph_2Pb){Fe(CO)_3NO}_2]$	2070 (3.4) , 2054 (10) , 2017 (1.8) , 2011 (2.1) , 1994sh 1991 (4.0) 1988sh	1793 (1·2), 1780sh, 1771 (2·4), 1753sh			
$ \begin{array}{l} [(Ph_2Sn)\{Fe(CO)_2(NO)[P(OPh)_3]\}_2] \stackrel{a}{=} \\ [(Ph_2Sn)\{Fe(CO)_2(NO)(AsEt_2Ph)\}_2] \stackrel{a}{=} \end{array} \end{array} $	2012 $(3 \cdot 4)$, 1997 $(4 \cdot 1)$, 1954 (10) , 1940sh 1990 $(3 \cdot 4)$, 1976 $(3 \cdot 8)$, 1970sh, 1930 (10) ,	1767sh, 1748 (5·3) 1761sh, 1743sh, 1728sh,			
$[(\mathrm{Ph_2Pb})\{\mathrm{Fe(CO)_2(NO)(AsEt_2Ph)}\}_2] \ ^{a}$	1923sh, 1916sh 2002sh, 1988 (3·2), 1970 (4·4), 1966sh, 1929 (10), 1923sh, 1916sh	1724 (5·5), 1718sh 1761sh, 1741sh, 1725sh, 1721 (5·6), 1716sh			
	^a Carbon disulphide solution.				

include derivatives of $[Fe(CO)_2(NO)_2]$. Their absorption bands are not included in Tables 2 and 3.

The reaction of tin(IV) halides with complexes containing mercury-transition-metal bonds provides a new and useful route to compounds having one tin-metal bond.²⁸ The reactivity of the halide appears to decline along the series $SnCl_4 > SnBr_4 > PhSnCl_3 > Ph_2SnCl_2 > Ph_3SnCl_3$ and increasingly vigorous conditions are required. Under these circumstances, both products and reactants decompose, and yields therefore decrease. A study of the reaction of $SnCl_4$ and $[Hg{Fe(CO)_3NO}_2]$ in benzene at room temperature shows that with a 1:1 mole ratio of the reactants, only one Fe-Hg bond is cleaved, and the reaction mixture contains [ClHgFe(CO)₃(NO)] and $[(Cl_3Sn)Fe(CO)_3(NO)]$. The former then reacts with more $SnCl_4$ to give the trichlorotin derivative, and, presumably, mercury(II) chloride. Only the first stage of the reaction of $SnBr_4$ with $[Hg{Fe(CO)_3NO}_2]$ takes place in benzene solution, but in hexane, the [BrHgFe- $(CO)_3(NO)$ formed disproportionates to HgBr₂ and $[Hg{Fe(CO)_3NO}_2]^{25}$ and finally $[(Br_3Sn)Fe(CO)_3(NO)]$ is obtained as the only product.

Diffraction studies have shown that in [(H₃Si)Co- $(CO)_{4}$],¹⁹ [(F₃Si)Co(CO)₄],¹⁶ and [(Cl₃Si)Co(CO)₄] ²¹ there is trigonal bipyramidal co-ordination about the cobalt atom with the silicon atom occupying an axial coordination position. Similar structures have been suggested for other $[(R_3M)Co(CO)_4]$ derivatives (M = Ge, Sn, and Pb)⁷ on the basis of their i.r. spectra and it is probable that a similar ligand distribution is found in their isoelectronic analogues described here. The presence of a single absorption band which may be assigned to a $\nu(NO)$ vibration in the spectra of the $[(R_3M)Fe$ - $(CO)_3(NO)$ complexes suggests that they do not exist as mixtures of isomers, and as they have three i.r.-active $\nu(CO)$ modes, structures of C_{3v} symmetry may be discounted. The suggested structure (Figure) is thus similar to that found in [(Ph₃P)Mn(CO)₃(NO)] ²⁹ with one nitrosyl and two carbonyl ligands occupying the three equatorial co-ordination positions of a trigonal bipyramid. The substituted compounds $[(R_3M)Fe(CO_2)-(NO)(PPh_3)]$ show only one v(NO) absorption band, and so isomerism is not likely. The relative intensities of the two absorption bands due to v(CO) modes * indicate an OC-Fe-CO angle of *ca*. 120°.³⁰ Thus it is suggested that the axial carbonyl ligand of the unsubstituted compounds has been replaced by a Ph₃P, or (PhO)₃P, ligand. A similar molecular geometry has been found in $[(Ph_3P)_2Mn(CO)_2(NO)]$,³¹ and $[(Ph_3Ge)Co(CO)_3(PPh_3)]$,¹⁵



The suggested structure for $[(\mathrm{R_3MFe})(\mathrm{CO})_2(\mathrm{NO})L]$ complexes

and has been suggested for other $[(R_3M)Co(CO)_3(PPh_3)]$ derivatives on the basis of their i.r. spectra.⁷

In those compounds such as $[(PhCl_2Sn)Fe(CO)_3(NO)]$ or $[(Ph_3Sn)Fe(CO)_2(NO)(AsEt_2Ph)]$ in which one of the axial groups is of the type $R^1R^2_2M$, two absorption bands are observed which are due to v(NO) modes. At the same time, more v(CO) absorption bands are present than would be expected. We suggest that this may be attributed to isomers of these compounds arising from restricted rotation about the Fe-Sn or Fe-As bonds. Their presence indicates that even in the unsubstituted compounds the nitrosyl ligand occupies an equatorial co-ordination position.

It is probable that the complexes of type $[(Ph_2M)-{Fe(CO)_2(NO)L}_2]$ [M = Sn or Pb; L = CO, (PhO)_3P, or PhEt₂As] also have trigonal bipyramidal co-ordination about the iron atoms with one apex occupied by a tin or lead atom and the other by the group L. They are less stable than the derivatives containing one M-Fe bond, and in solution decompose to give [LFe(CO)(NO)_2] and [(Ph_3M)Fe(CO)_2(NO)L]. Thus, although the i.r. spectra ³⁰ W. Beck, A. Melnikoff, and R. Stahl, *Chem. Ber.*, 1966, **99**, 3721.

³¹ J. H. Enemark and J. A. Ibers, Inorg. Chem., 1967, 6, 1575.

^{*} That at higher frequency is assigned to the symmetric ν (CO) vibration and the other to the asymmetric mode (see ref. 30 and references therein).

²⁸ M. Casey and A. R. Manning, Chem. Comm., 1970, 674.

²⁹ J. H. Enemark and J. A. Ibers, Inorg. Chem., 1968, 7, 2339.

of the unsubstituted and tertiary arsine compounds show more than the two $\nu(NO)$ absorption bands expected, these may be due to decomposition products. It is noticeable that the most stable compound $[(Ph_2Sn)-\{Fe(CO)_2(NO)[P(OPh)_3]\}_2]$ shows only two $\nu(NO)$ and four $\nu(CO)$ bands. Consequently although isomerism of the type discussed above is possible in these complexes, its occurrence is not proven.

The frequencies of the $\nu(CO)$ and $\nu(NO)$ vibrations of the compounds described here vary with R, M, and L. The variations are similar to those noted for the $\nu(CO)$ modes of the isoelectronic complexes which contain the $Co(CO)_{a}L$ groups.^{7,8}

In solution in acetonitrile, the trihalogenotin and trichlorogermanium derivatives decompose rapidly. However, the $[(R_3M)Fe(CO)_3(NO)]$ and $[(R_2M){Fe(CO)_3}(NO)]_2]$ complexes (R = Ph or alkyl; and M = Sn or Pb) dissociate completely and reversibly to give $[Fe(CO)_3NO]^-$ and, presumably, solvated $[R_3M^+]$ and $[Ph_2M]^{2+}$ ions. The anion may be identified by the absorption bands due to its v(NO) and v(CO) vibrations [1646 (4·2), 1884 (10), and 1986 (2·8) cm⁻¹; cf. ref. 25]. In tetrahydrofuran, a partial dissociation is observed, but there is no evidence for the formation of the

 $[(Ph_2M)Fe(CO)_3(NO)]^+$ ions. Similar behaviour has been reported for many compounds containing metal-metal bonds,³² and it is interesting to compare the $[(Ph_2M)-{Fe(CO)_3(NO)}_2]$ compounds with $[Hg{Fe(CO)_3(NO)}_2]^{.25}$. The mercury derivative does not dissociate in tetrahydrofuran solution and dissociates only partially in acetonitrile. Thus, for any given solvent the degree of dissociation of $[M{Fe(CO)_3(NO)}_2]$ derivatives decreases along the series $M = Ph_2Sn > Ph_2Pb > Hg$. This may be due to changes in the M-Fe bond energies or to variations in the solvation energies of the M²⁺ ions.

The substituted compounds $[(R_3M)Fe(CO)_2(NO)L]$ and $[(Ph_2M){Fe(CO)_2(NO)L}_2]$ do not dissociate in either tetrahydrofuran or acetonitrile solution. However, the triphenyl phosphite derivative $[(Ph_2Sn){Fe(CO)_2(NO)-[P(OPh)_3]}_2]$ undergoes a slow, complex reaction with acetonitrile to give the $[Fe(CO)_3NO]^-$ ion as a final product. However, the absorption bands due to acetonitrile obscure absorption bands of the solute with frequencies < ca. 1680 cm⁻¹. We were therefore unable to investigate this reaction further.

[0/1372 Received, August 10th, 1970]

32 J. M. Burlitch, J. Amer. Chem. Soc., 1969, 91, 4562.