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A MÖSSBAUER STUDY OF [(TRICARBONYLTRIPHENYLSTIBINEPHENYLIRON)-DIPHENYLSTIBINE] TETRACARBONYLIRON, $Ph_3Sb(CO)_3PhFePh_2SbFe(CO)_4$

DAVID J. CANE *, ERIC J. FORBES ** and JACK SILVER ***

Department of Chemistry, University of Birmingham, P.O. Box 363, Birmingham B15 2TT (Great Britain)

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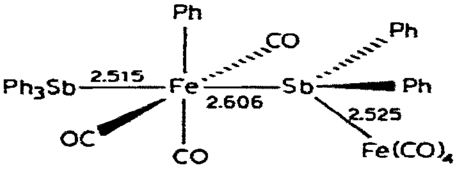
Summary

The ^{57}Fe and ^{121}Sb Mössbauer spectra of $Ph_3Sb(CO)_3PhFePh_2SbFe(CO)_4$ (A) have been recorded. The ^{57}Fe spectra of $Ph_3SbFe(CO)_4$ and of A have been recorded in a magnetic field. The implications of these results for the nature of the iron—antimony bond in compound A is discussed.

The ^{57}Fe Mössbauer effect in $Fe(CO)_5$ and its derivatives has been the subject of many investigations [1—9]. These have included results for mono- and for disubstituted compounds with Ph_3D (D = P, As and Sb) [1—3]. Since the Mössbauer effect can be observed with ^{121}Sb, $Ph_3SbFe(CO)_4$ and $(Ph_3Sb)_2Fe(CO)_3$ have been studied by a double Mössbauer experiment [10]. This technique has also yielded interesting results for compounds containing iron—tin bonds [11,12]. We report here a ^{57}Fe and ^{121}Sb Mössbauer study of $Ph_3SbFe(CO)_4$ (I) and of an interesting compound containing both a penta- and a hexa-coordinate iron atom. $Ph_3Sb(CO)_3PhFePh_2SbFe(CO)_4$ (II). For both these compounds we also report the ^{57}Fe spectra recorded in a magnetic field of 6 T. The Mössbauer data for com-

$Ph_3SbFe(CO)_4$

(I)



(II)

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* Current address: Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada, T6G 2G2.
** To whom correspondence should be addressed.
*** Current address: Department of Chemistry, University of the West Indies, St. Augustine, Trinidad.

pound I, although already reported [10], was reinvestigated since the antimony and iron environments are similar to those of two of the sites in compound II. The structure of compound II was revealed by an X-ray diffraction study [13].

Experimental

The ^{57}Fe and ^{121}Sb Mössbauer spectra at 4.2 K were obtained through the P.C.M.U. Services of A.E.R.E. Harwell. The ^{121}Sb spectra for compounds I and II are given in Fig. 1 and 2 respectively; the ^{57}Fe spectrum for compound II is given in Fig. 3. The room temperature (298 K) spectrum of compound I (not shown, but results quoted in Table 2) was obtained using apparatus previously described [14].

The ^{57}Fe spectrum for compound I in a magnetic field of 6 T (Fig. 4) is not fitted but it is seen by inspection that ΔE_Q is positive and $\eta = 0$. This information was used as a starting set to fit the spectrum for compound II. This latter spectrum (Fig. 5) has a normalized sum of squares equal to 278 for 242 degrees of freedom. The data for compound II were fitted (Fig. 6) by Dr. B.W. Dale (A.E.R.E., Harwell) using a modified version of the programme reported by Lang and Dale [15].

Results for ^{121}Sb are quoted in Table 1, those for ^{57}Fe are quoted in Table 2.

Results and discussion

There is a large change (—1.29 to +1.68 at 4 K) in the ^{121}Sb chemical shift upon complexing Ph_3Sb to $Fe(CO)_4$ (compound I). This corresponds to a change

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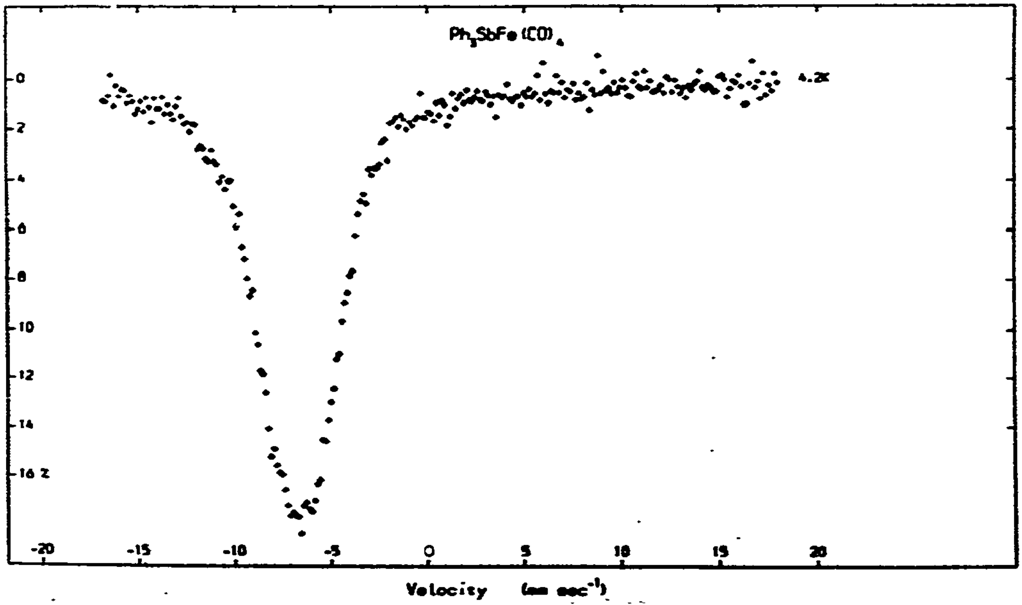

Fig. 1. ^{121}Sb spectrum of compound I. (Source Ba^{121}SnO$_3$, 4.2 K)

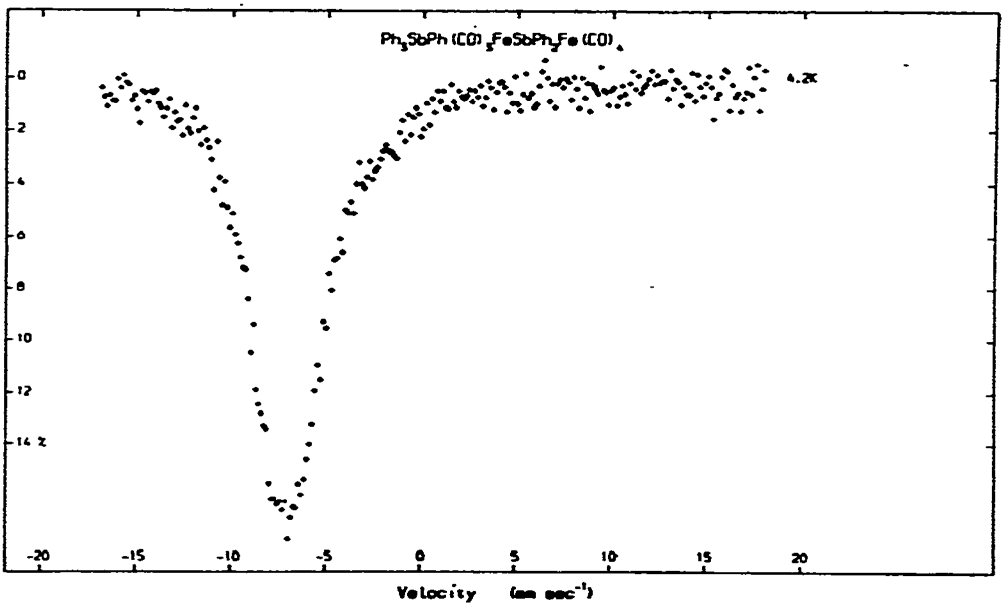

Fig. 2. ^{121}Sb spectrum of compound II. (Source Ba ^{121}SnO$_3$, 4.2 K.)

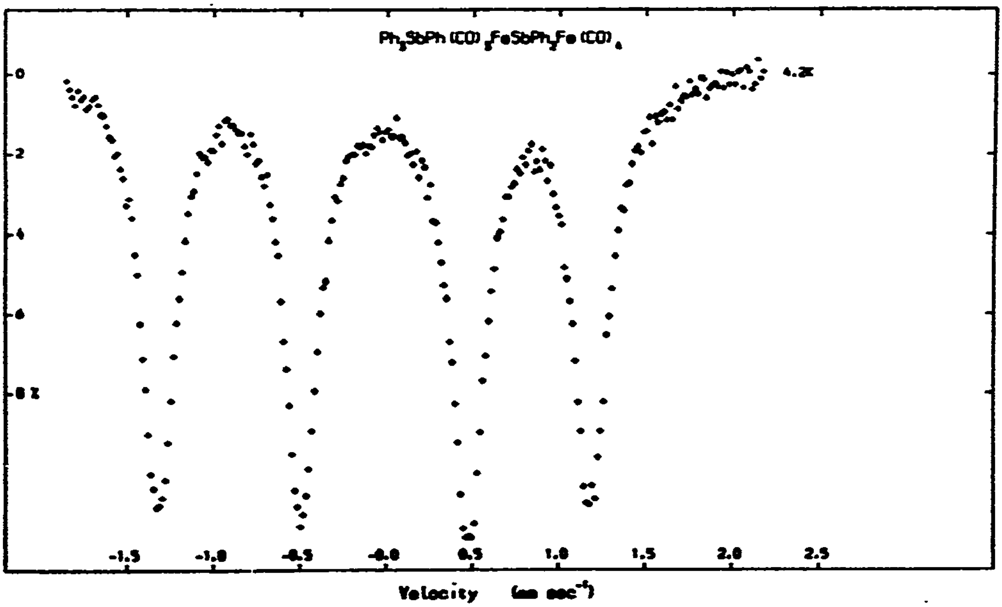

Fig. 3. ^{57}Fe spectrum of compound II at 4.2 K. (Source Rh^{57}Co, 300 K.)

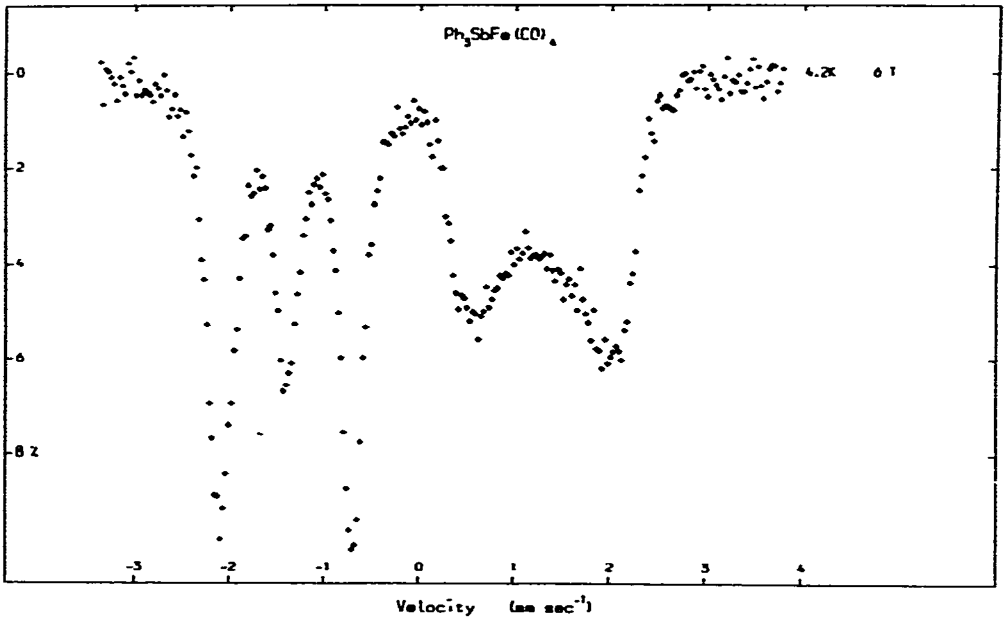

Fig. 4. ^{57}Fe spectrum of compound I in a magnetic field of 6 T. (Source Rh ^{57}Co, 300 K.)

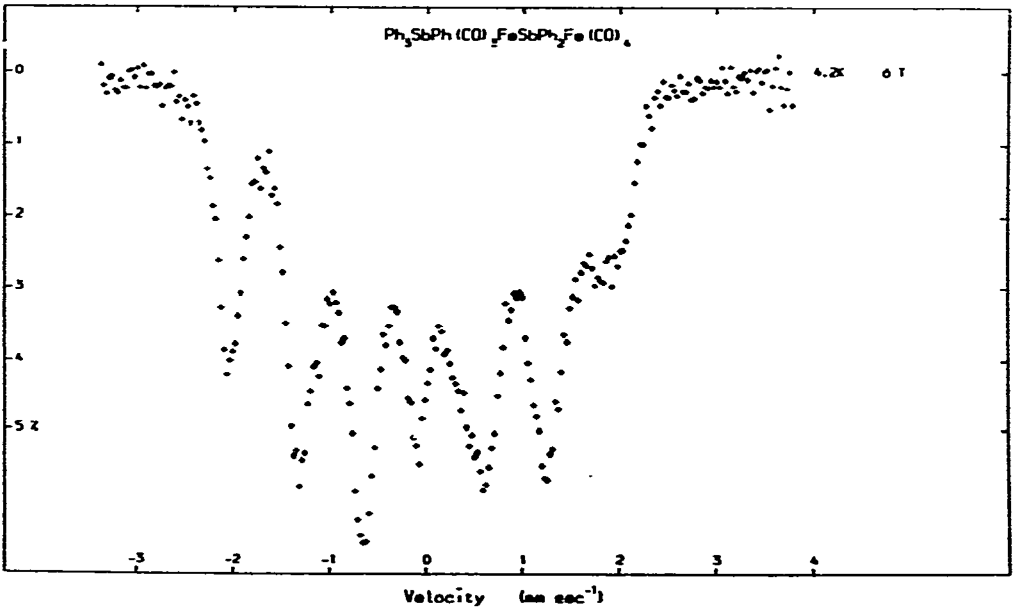

Fig. 5. ^{57}Fe spectrum of compound II in a magnetic field of 6 T. (Source Rh^{57}Co, 300 K.)

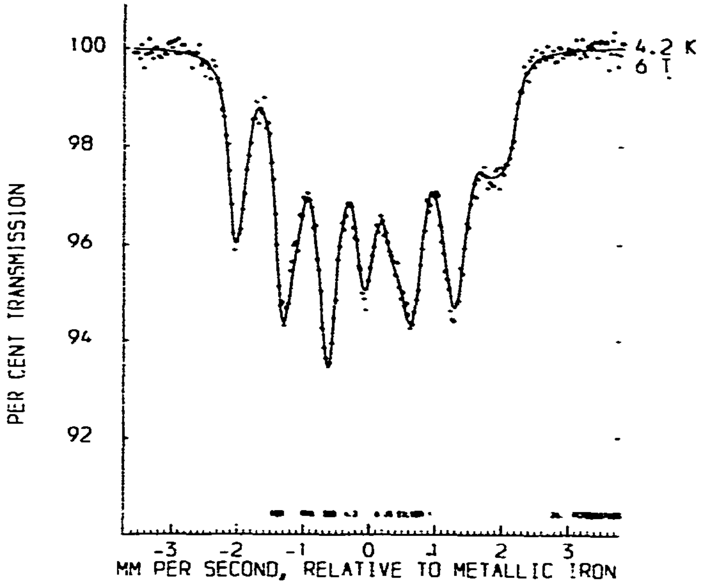

Fig. 6. Fitted spectrum of compound II in a magnetic field of 6 T.

TABLE 1

^{121}Sb MÖSSBAUER PARAMETERS

	Temp. (K)	Width (mm s^{-1})	δ [a] (mm s^{-1})	e^2qQ (mm s^{-1})	Ref.
Ph_3Sb	80	3.2 ± 0.4	—0.9 ± 0.02	17 ± 2	10
	4.2	2.8 ± 0.2	—1.2 ± 0.02	17.5 ± 0.1	10
$Ph_3SbFe(CO)_4$	80	3.0	2.82 ± 0.2	16 ± 2	10
	4.2	3.26 ± 0.6	1.68 ± 0.02	9.0 ± 0.03	10
	4.2	3.3 ± 0.3	1.67 ± 0.03	9.2 ± 0.03	b
$Ph_3Sb(CO)_3PhFePh_2SbFe(CO)_4$ [c]	4.2	~2.7	~1.6		b

[a] Isomer shifts quoted relative to InSb. [b] This work. [c] Not fitted.

TABLE 2

^{57}Fe MÖSSBAUER PARAMETERS

	Temp. (K)	δ (mm s^{-1})	e^2qQ (mm s^{-1})	η	Ref.
$Ph_3Fe(CO)_4$	80	0.10 ± 0.01	2.67 ± 0.01		10
	295	0.15 ± 0.03	2.63 ± 0.03		10
	295	—0.14 ± 0.03	2.63 ± 0.03		a
$Ph_3Sb(CO)_3PhFe^*Ph_2SbFe^{**}(CO)_4$	4.2	Fe^* 0.01	—0.96	0.475	a
		Fe^{**} —0.56	2.49	0.2	a

[a] This work relative to natural Fe. Ref. 10 data relative to $Na_2Fe(CN)_5NO \cdot 2H_2O$ at 295 K.

in valency from antimony(III) to antimony(V) [16,17]. A σ-donation from the antimony lone pair to iron was put forward as the explanation [10] for the change in δ(Sb) which is reasonable if the bond angles in Ph_3Sb are less than 120° *.

Additional support for a σ-bonding scheme is seen in the quadrupole coupling data. Bowen et al. [10] have reported a positive sign for e^2qQ in triphenylstibine which corresponds to an excess of 5*p* electrons along the threefold symmetry axis (z axis) [17]. The fact that the sign of e^2qQ remains positive upon complexing to form $Ph_3SbFe(CO)_4$ (I) indicates that there is no large increase in the 5*p* population along the x and y axes. A π-back donation from iron would primarily increase the p_x and p_y densities [10]. If this were a major interaction the sign of e^2qQ should become negative, but as pointed out by Bowen et al. [10] a reduction in magnitude (from +17 to ca. +10 mm s^{-1}) is consistent with a σ-donation along the z-axis from a hybrid orbital with some *p*-character.

The ^{121}Sb spectrum of compound II shown in Fig. 2 has not been fitted to two antimony sites as it is felt that it would not yield a conclusive result. It does show that the environments of the two antimony atoms are similar. By inspection the spectrum is seen to have a line-width of about 2.7 mm s^{-1} and shows a chemical shift of about 1.6 mm s^{-1}. Since the line-width is narrower than that of compound I, it suggests that there is a further reduction in the magnitude of e^2qQ in going from compound I to compound II. This is again consistent with more σ-donation along the z-axis from a hybrid orbital with some *p*-character, and this agrees with the known crystal structure of compound II where the Ph_3Sb entity is bonded to an iron environment that is hexacoordinate [13].

The other antimony atom in compound II has two bonds to iron and two to phenyl in a distorted tetrahedral arrangement. Since the total spectrum has a narrow line-width there is only a small quadrupole splitting indicating a symmetric environment with predominant σ-bonds (two σ-bonds to phenyl, one to iron and a σ-donation to $Fe(CO)_4$) which is in agreement with the crystal structure [13]. In fact the Mössbauer data for compound II indicates an electronic environment that is more symmetrical than the crystallographic environment.

The first feature of interest in the ^{57}Fe results (reported in Table 2) is that there is only a small difference in the Mössbauer parameters between the pentacoordinate iron sites in compounds I and II. For compound II the e^2qQ is smaller and this is probably due to more σ-electron density in the iron—antimony bond, which would indicate that $Ph_3Sb(CO)_3PhFeSbPh_2$ is a better σ-donor than Ph_3Sb. This is consistent with the iron—antimony bond in the former being more electron-donating than the iron—phenyl bond in the latter. Further evidence for this is seen in the chemical shifts where that of compound I is less than that of compound II.

The other iron site in compound II gives a smaller quadrupole splitting compatible with the hexacoordination found in the crystal structure. The Mössbauer data for this site are similar to those found for iron in the compound $I(CO)_3Fe(PMe_2)_2Fe(CO)_3I$ (e^2qQ = 0.99 mm s^{-1}, δ = −0.001 mm s^{-1}) which is known to be hexacoordinate [19]. The bonding around the iron atoms of this latter com-

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* Although the C—Sb—C bond angles in Ph_3Sb have not been measured there is every expectation that they will be much less than 120°, and Campbell [18] has made an estimate of 113°.

pound is similar to that around the hexacoordinate iron site in compound II, comprising of CO-ligands and three formal σ-bonds. The octahedral iron atom in compound II is bonded to three CO ligands, a σ-donor (Ph_3Sb) and two pure σ-bonds to phenyl and the $SbPh_2Fe(CO)_4$ moiety. A value of 0.4 is found for η.

Conclusions

The two antimony sites in compound II have similar environments. The atoms are σ-bonding towards the iron atoms and may be regarded as antimony(V) ions. Their electronic environments appear to be more symmetrical than their crystallographic environments.

The ^{57}Fe Mössbauer data for the pentacoordinate site is typical of other derivatives of iron pentacarbonyl. The other iron site is unusual and gives Mössbauer parameters consistent with its octahedral environment. The value of η found for this site is on the verge of significance, but more data on other hexacoordinate iron carbonyl environments is needed before more information can be obtained from the η value.

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References

1 R.L. Collins and R. Pettit, J. Chem. Phys., 39 (1963) 3433.
2 R.L. Collins and R. Pettit, J. Amer. Chem. Soc., 85 (1963) 2332.
3 R.H. Herber, R.B. King and G.K. Wertheim, Inorg. Chem., 3 (1964) 101.
4 L. Korecz and K. Burger, Acta Chim. (Budapest), 58 (1968) 253.
5 W.R. Cullen, D.A. Harborne, B.V. Liengme and J.R. Sams, Inorg. Chem., 8 (1969) 1464.
6 R.E. Dessy, J.C. Charkoudian, T.P. Abeles and A.L. Rheingold, J. Amer. Chem. Soc., 92 (1970) 3947.
7 M. Kalrius, U. Kahn, P. Kienle and H. Eicher, Z. Naturforsch. A, 17 (1962) 494.
8 R. Greatrex and N.N. Greenwood, Discuss. Faraday Soc., No. 47 (1969) 126.
9 K. Farmerg, M. Kilner, R. Greatrex and N.N. Greenwood, J. Chem. Soc. A, (1969) 2339.
10 L.H. Bowen, P.E. Garrou and G.G. Long, Inorg. Chem., 11 (1972) 182.
11 D.E. Fenton and J.J. Zuckerman, J. Amer. Chem. Soc., 90 (1969) 6226.
12 W.R. Cullen, J.R. Sams and J.A.T. Thompson, Inorg. Chem., 10 (1971) 343.
13 D.J. Cane, E.J. Forbes and T.A. Hamor, J. Organometal. Chem., 117 (1976) C101.
14 J. Silver and J.D. Donaldson, Inorg. Nucl. Chem. Lett., in press.
15 G. Lang and B.W. Dale, Nucl. Instrum. Meth., 116 (1974) 567.
16 S.L. Ruby in I.J. Gruverman (Ed.), Mossbauer Effect Methodology, Vol. 3. Plenum Press, New York, 1967.
17 G.G. Long, J.G. Stevens, R.J. Tullbane and L.H. Bowen J. Amer. Chem. Soc., 92 (1970) 4230.
18 I.G.M. Campbell, J. Chem. Soc., (1955) 3116.
19 T.C. Gibb, R. Greatrix, N.N. Greenwood and D.T. Thompson J. Chem. Soc. A, (1967) 1663.