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^{121}Sb, ^{57}Fe and ^{127}I Mössbauer spectroscopic study on antimony-transition metal bond in metal carbonyl derivatives of tertiary stibines

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Abstract

Antimony-transition metal bonds in five- or six-coordinate $[M(CO)_n(SbR_3)]$ ($M = Fe$, Ru; $n = 4$, $M = Cr$, Mo, W; $n = 5$, $R = Me$, Ph), seven-coordinate $[MI_2(CO)_3(SbPh_3)L]^-$ ($M = Mo$, W, $L = PPh_3$, $AsPh_3$) and $[MI_3(CO)_3(SbPh_3)]^-$ ($M = Mo$, W) have been investigated using the ^{121}Sb, ^{57}Fe and ^{127}I Mössbauer spectroscopy. Coordination of SbR_3 to the transition metal atom results in the increase in the values of isomer shift and the decrease in the values of quadrupole coupling constant of the ^{121}Sb Mössbauer spectra. This indicates that the lone pair electron of the stibine is transferred to the transition metal atom. The degree of the transfer increases in the order of $Mo < W < Ru$, and $Cr \ll Fe$, being the order of the Allred–Rochow's electronegativity for the transition metal atom. The same trend holds for $[MI_2(CO)_3(SbPh_3)L]$ ($M = Mo$, W). ^{57}Fe Mössbauer spectra of $[Fe(CO)_4(SbR_3)]$ at 80 K are not so different from that of $Fe(CO)_5$, suggesting that some redistribution of electron density around Fe atom occurs. The ^{127}I Mössbauer spectra for $[MI_2(CO)_3(SbPh_3)L]$ and $[MI_3(CO)_3(SbPh_3)]$ show a typical σ interaction in M–I bonds.

Keywords: Mössbauer spectroscopy; Metal carbonyl complex; Stibine complex; Electron distribution; Antimony-transition metal bond; σ-donation

1. Introduction

The complexes having a bond between d-block and heavy p-block elements have attracted considerable interests [1]. The transition metal complexes of tertiary phoshine ligands have been intensively studied in organometallic chemistry. In contrast, the coordination chemistry of the heavier Group 15 analogues, stibines, have received limited attention [2], partly due to their weak coordination ability. The lack of adequate NMR probe nucleus in stibines such as ^{31}P in phosphines has also prevented extensive investigation. For the antimony compounds the electronic state can, however, be elucidated by means of ^{121}Sb Mössbauer spectroscopy. Since the Mössbauer spectra give information on the electron distribution around the Mössbauer atom, we can extract the information on the chemical bond. ^{121}Sb Mössbauer spectroscopy is a powerful tool for such purpose as we have demonstrated in the hypervalent compounds [3] and the organometallic compounds [4].

Although ^{57}Fe Mössbauer spectroscopy has been applied extensively to the iron carbonyl compounds, a few number of double Mössbauer spectroscopic studies have been reported. The Mössbauer spectroscopic studies on the Sb–Fe bond using both ^{121}Sb and ^{57}Fe Mössbauer resonances have been conducted for several compounds; ie. $[Fe(CO)_4(SbPh_3)]$ [5], $[Fe(CO)_3(SbPh_3)_2]$ [5], $[X_nSb\{Fe(CO)_2(\pi\text{-}C_5H_5)\}_{4-n}]^+$ ($X = Cl$, Br, I, CF_3, C_6H_5, C_4H_9, $n = 1–3$) [6], $Ph_3Sb(CO)_3PhFePh_2\text{-}SbFe(CO)_4$ [7], $[Et_4N]_2[HSb\{Fe(CO)_4\}_3]$ and $[Et_4N]_3[Sb\{Fe(CO)_4\}_4]$ [4]. In contrast to the compounds above, only one ^{121}Sb Mössbauer spectrum of the carbonyl complexes having Sb bonded to a transition metal other than Fe was measured for $[Sb\{Co(CO)_3PPh_3\}_4][PF_6]$ [6].

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In this paper, we report the ^{121}Sb, ^{57}Fe and ^{127}I Mössbauer spectra for transition metal carbonyl species with SbR_3 (R = Me, Ph), i.e. $[M(CO)_4(SbR_3)]$ (M = Fe, Ru; R = Me, Ph), $[M(CO)_5(SbR_3)]$ (M = Cr, Mo, W; R = Me, Ph), and $[MI_2(CO)_3(SbPh_3)L]$ (M = Mo, W; L = PPh_3,$AsPh_3$) and $[NBu_4][MI_3(CO)_3(SbPh_3)]$ which have five, six and seven coordination, respectively. We took them up for a systematic investigation of the interaction between the d-block elements with 3d, 4d and 5d electrons and the heavy p-block element with 5s and 5p valence electrons. The acceptor strength of the d-block element is especially highlighted. A number of studies from such a view point have been carried out [8–10]. The metal carbonyl complexes are good for a systematic study on the behavior of the d-block elements as Lewis acids.

2. Experimental

All manipulations were performed under an inert atmosphere of N_2 or Ar using a standard Schlenk and vacuum line techniques, or using a glove box under a high purity nitrogen atmosphere. Solvents were dried by the conventional methods and deoxygenated. $[Fe(CO)_4(SbMe_3)]$ [11] $[Fe(CO)_4(SbPh_3)]$ [12], $[Ru(CO)_4(SbPh_3)]$ [13], $[M(CO)_5(SbPh_3)]$ (M = Cr, Mo, W) [14], $[MI_2(CO)_3(SbPh_3)L]$ and $[Bu_4][MI_3(CO)_3(SbPh_3)]$ [15] were prepared by the literature methods.

2.1. Synthesis of $[Ru(CO)_4(SbMe_3)]$

A mixture of $[Ru_3(CO)_{12}]$ (1.9 g, 4 mmol) and trimethylstibine [16] (1.5 g, 9 mmol, ether solution) in hexane (250 cm^3) was irradiated with a 1 kW mercury arc lamp at 25°C. When the reaction was completed (4 h), the solution was filtered and the solvent was evaporated to dryness. The residue was purified by a vacuum sublimation at 80°C using an oil-rotary pump. (98 mg, 2.8% yield): Orange powder. IR (in hexane, cm^{-1}): 2071, 2058, 1988, 1965, 1952.

2.2. Synthesis of $[M(CO)_5(SbMe_3)]$ (M = Cr, Mo)

A solution of $[Cr(CO)_5(thf)$ (THF = tetrahydrofuran) in THF, prepared by the photolysis of $[Cr(CO)_6]$ (20 mmol) in THF (250 cm^3) [17], was added to an ether solution of trimethylstibine (3.2 g, 20 mmol), and the mixture stirred in an ice–water bath for 4 h. After filtration, solvent was removed under vacuum. The oily product was dried in vacuo and purified by a vacuum sublimation at 60°C (2.56 g, 35.7% yield): Yellow crystals. IR (Nujol mull, cm^{-1}): 2058 s, 2001 sh, 1938 vs.

The molybdenum complex $[Mo(CO)_5SbMe_3)]$ was prepared in the same manner (1.82 g, 15.9% yield). IR (Nujol mull, cm^{-1}): 2069 m, 1947 vs. Anal. Calc. for $C_8H_9MoO_5Sb$: C, 23.85; H, 2.25. Found: C, 23.98; H, 2.87%.

2.3. Synthesis of $[W(CO)_5(SbMe_3)]$

A mixture of $W(CO)_6$ (4.22 g, 0.012 mol), trimethylstibine (3.2 g, 20 mmol) and diethylene glycol dimethyl ether (50 cm^3) was heated to reflux for 6 h. The reaction mixture was allowed to cool, filtered and the solvent was removed by the distillation under reduced pressure. The residue was dried by in vacuo and purified by a vacuum sublimation at 60°C (0.31g, 5.3% yield). IR (Nujol mull, cm^{-1}): 2068 m, 1938 vs, 1901 m. Anal. Calc. for $C_8H_9O_5SbW$: C, 19.58; H, 1.85. Found: C, 19.63; H, 1.96%.

2.4. ^{121}Sb Mössbauer spectra [18]

The ^{121}Sb Mössbauer spectra were measured with an Austin Science S-600 spectrometer using a $Ca^{121m}SnO_3$ source (16 MBq) and a germanium detector. Both the sample containing 15 mg Sb cm^{-2} and the source were kept at 20 K in a cryostat equipped with a closed-cycle refrigerator. The Doppler velocity was measured with an Austin Science LA-9 laser interferometer and calibrated by measuring a ^{57}Fe Mössbauer spectrum of α-iron foil at 20 K. The ^{121}Sb Mössbauer spectra were computer-fitted to quadrupole-split twelve-lines using a transmission-integral method [19]. The values of isomer shift, δ_{Sb} are referred to that of InSb at 20 K.

2.5. ^{57}Fe Mössbauer spectra

The ^{57}Fe Mössbauer spectra were obtained using a Mössbauer driving system from WissEl GmbH, consisting of an MDU-1200 Mössbauer driving unit, a DFG-1200 digital function generator and an MVT-1000 velocity transducer, incorporating with a model 5500 multichannel analyser from EG&G ORTEC. The samples containing 6 mg Fe cm^{-2} were kept at 80 K in a CF1 104 continuous gas flow cryostat from Oxford Instruments and the ^{57}Co (Rh) source (1.5 GBq) kept at r.t. The spectra were computer fitted to Lorentzian lines on a personal computer and the values of isomer shift, δ_{Fe}, are given relative to α-iron foil at r.t.

2.6. ^{127}I Mössbauer spectra [20]

The Mg_3 $^{127m}TeO_6$ Mössbauer source was prepared by a high-flux neutron irradiation in a reactor core of JRR-3M of Japan Atomic Energy Research Institute. ^{127}I Mössbauer spectra were measured using an Austin Science S-600 Mössbauer controller coupled with a Norland-ORTEC IT-5600 multichannel analyser. Both the Mössbauer source (1.5 GBq) and samples contain-

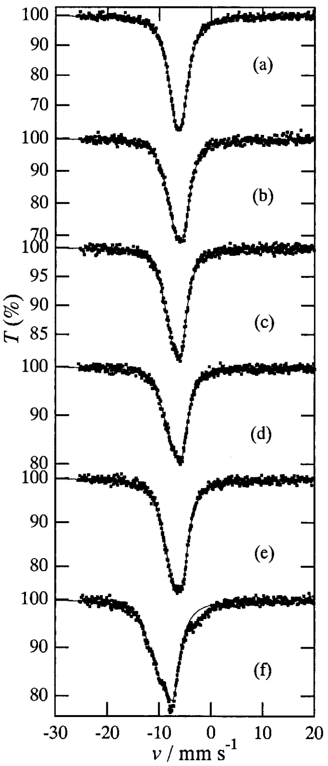


Fig. 1. ^{121}Sb Mössbauer spectra for [M(CO)$_4$(SbMe$_3$)] (M = Fe, Ru; a, b) and [M(CO)$_5$(SbPh$_3$)] (M = Cr, Mo, W; c–e) and SbMe$_3$ (f) at 20 K. The metal atoms are; (a) Fe, (b) Ru, (c) Cr, (d) Mo, (e) W.

ing 30 mg I cm^{-2} were kept at 20 K in a cryostat with a closed-cycle refrigerator. The 57.6 keV Mössbauer γ-rays were detected by a pure germanium detector. The Doppler velocity of the source was measured with an Austin LC-9 laser interferometer and calibrated by measuring the ^{57}Fe Mössbauer spectrum of an α-iron foil at 20 K using a ^{57}Co(Rh) source. The ^{127}I Mössbauer spectra were computer-fitted to quadrupole-split 12-lines using the transmission-integral method [19]. The values of the isomer shift, δ_I, are given relative to KI at 20 K.

3. Results and discussion

3.1. Five- or six-coordinate complexes [M(CO)$_n$(SbR$_3$)] (M = Fe, Ru; n = 4, M = Cr, Mo, W; n = 5, R = Me, Ph)

Fig. 1 shows the ^{121}Sb Mössbauer spectra for [M(CO)$_n$(SbMe$_3$)] (M = Fe, Ru, $n = 4$; M = Cr, Mo, W, $n = 5$) and SbMe$_3$. The weak shoulder-like absorption observed in SbMe$_3$ is due to impurities formed by the air-oxidation during the Mössbauer sample preparation. Essentially the same spectra have been obtained for corresponding SbPh$_3$ complexes. The absorption line shape for [M(CO)$_n$(SbR$_3$)] were more symmetric than those for free SbR$_3$. The change in absorption shape clearly indicates that the values of quadrupole coupling constant $(e^2qQ)_{Sb}$ become small on coordination, suggesting that the donation of the lone pair of SbR$_3$ to the transition metal occurs as discussed later.

The ^{121}Sb Mössbauer parameters are summarized in Table 1. Coordination of SbR$_3$ to the metal atom leads to the increase in the values of δ_{Sb}, and the decrease in those for $(e^2qQ)_{Sb}$. The increase in δ_{Sb} indicates the decreases in the Sb 5s electron density. This clearly shows a σ donation of the Sb lone pair to the transition metal atom. The decrease in $(e^2qQ)_{Sb}$ on coordination

Table 1
^{121}Sb Mössbauer parameters for carbonyl complexes at 20 K

Number	Compound	δ_{Sb} (mm s^{-1}) [a]	(e^2 qQ)$_{Sb}$ (mm s^{-1})	η	Γ_{exp} (mm s^{-1})
1	[Fe(CO)$_4$(SbMe$_3$)]	2.28	5.7	0.42	2.18
2	[Ru(CO)$_4$(SbMe$_3$)]	2.14	10.2	0.25	2.29
3	[Cr(CO)$_5$(SbMe$_3$)]	1.86	10.7	0.26	2.46
4	[Mo(CO)$_5$(SbMe$_3$)]	1.67	12.1	0.03	2.67
5	[W(CO)$_5$(SbMe$_3$)]	1.93	11.6	0.48	2.37
6	SbMe$_3$	−0.28	16.2	0.00	2.86
7	[Fe(CO)$_4$(SbPh$_3$)]	2.12	8.4	0.01	2.83
8	[Ru(CO)$_4$(SbPh$_3$)]	1.83	12.5	0.05	2.89
9	[Cr(CO)$_5$(SbPh$_3$)]	1.63	11.8	0.38	2.62
10	[Mo(CO)$_5$(SbPh$_3$)]	1.58	13.2	0.12	2.39
11	[W(CO)$_5$(SbPh$_3$)]	1.77	12.8	0.13	2.47
12	SbPh$_3$	−0.77	16.7	0.12	2.62
13	[MoI$_2$(CO)$_3$(SbPh)(PPh$_3$)]	1.63	9.7	0.06	2.46
14	[WI$_2$(CO)$_3$(SbPh$_3$)(PPh$_3$)]	1.65	7.8	0.00	2.71
15	[MoI$_2$(CO)$_3$(SbPh$_3$)(AsPh$_3$)]	1.70	8.7	0.00	2.45
16	[WI$_2$(CO)$_3$(SbPh$_3$)(AsPh$_3$)]	1.85	7.3	0.02	2.78
17	[NBu$_4$][MoI$_3$(CO)$_3$(SbPh$_3$)]	1.90	7.8	0.00	2.58
18	[NBu$_4$][WI$_3$(CO)$_3$(SbPh$_3$)]	1.90	8.9	0.00	2.37

[a] Relative to InSb at 20 K.

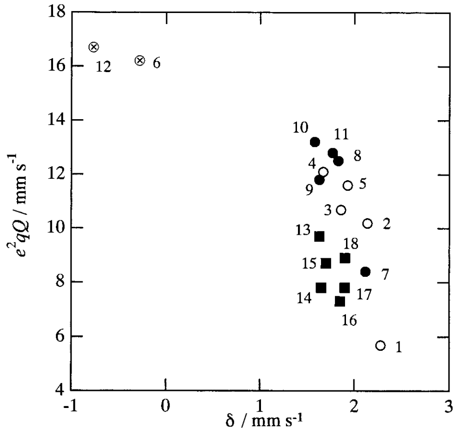


Fig. 2. Relationship between the values of δ_{Sb} and $(e^2qQ)_{Sb}$ for the carbonyl complexes with $SbMe_3$ (open circles) and $SbPh_3$ (solid circles), and seven-coordinate carbonyl complexes with $SbPh_3$ (solid squares). The Arabic numerals in the figure indicate the numbers for the compounds shown in Table 1.

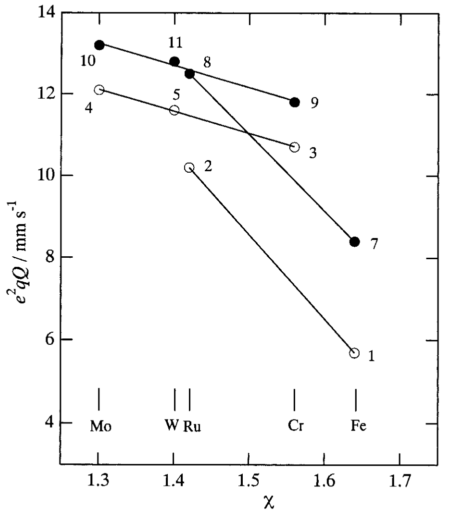


Fig. 3. Relationship between the values of ^{121}Sb Mössbauer parameters, $(e^2qQ)_{Sb}$ and Allred–Rochow's electronegativity of the transition metal in $[M(CO)_4(SbMe_3)]$ (open circles) and $[M(CO)_5 SbPh_3)]$ (solid circles). The Arabic numerals in the figure indicate the numbers for the compounds shown in Table 1.

indicates that the imbalance in the Sb 5p electron population decrease. Since the positive values of $(e^2qQ)_{Sb}$ in SbR_3 are due to p orbital character of the lone pair, the decrease implies a σ donation of the 5p electrons of the lone pair. Thus the changes in the values of both δ_{Sb} and $(e^2qQ)_{Sb}$ show that both 5s and 5p electrons of the lone pair are donated to the transition metal atom.

The back-donation from the transition metal atom would not be significant because the signs for the values of $(e^2qQ)_{Sb}$ are positive. If such an interaction were important, the negative value of $(e^2qQ)_{Sb}$ were observed since the back-donated electrons are considered to be engaged in the orbitals perpendicular to the lone pair, namely, p_x and p_y orbitals. The poor π-acidity for the stibine ligands is well-known and the same results have been concluded for other stibine complexes [5,10].

Fig. 2 shows the relation between the values of δ_{Sb} and $(e^2qQ)_{Sb}$. This plot is a measure of the relative electron density in the lone pair, namely, the less s electron density, the more rightward the point is plotted, and the less p_z electron density, the more downward. Fig. 2 indicates that 5s and $5p_z$ electron densities are changed in a parallel manner and the degree of the electron migration depends on the transition metal; both 5s and $5p_z$ electron densities are in the order of Ru > Fe for the Group 8 metals and Mo > W > Cr for the Group 6 metals. In other word, the degree of the change in 5s and 5p electron densities caused by the coordination increases in the order; Ru < Fe and Mo < W < Cr. Interestingly the order for Group 6 metals is not that of the period, being the parallel relation to the Sb–M bond length in $[M(CO)_5(SbMe_3)]$ [21] and $[M(CO)_5SbPh_3)]$ [22].

Fig. 3 is a plot of the values of $(e^2qQ)_{Sb}$, against the Allred–Rochow's electronegativity [23] of the metal atom χ. The values of $(e^2qQ)_{Sb}$, the degree of the electron migration in other words, is found to be strongly correlated with χ. Since the value of χ for Sb is 1.8, the difference between Sb and M is largest for molybdenum and smallest for iron. Taking into account the electronegativity, the Mössbauer parameters obtained are well explained by considering that the electron migration from antimony to iron atom is largest and consequently the Sb–Fe bond is most covalent, while that to molybdenum is smallest and most ionic among the complexes studied.

We can estimate the change in valence electron populations of the antimony atoms. The Mössbauer parameters, i.e. isomer shift, quadruple coupling constant and asymmetry parameter (η) are closely related to the electron configurations of the Mössbauer atom [8,24].

$$U_p = -\frac{e^2qQ}{(e^2qQ)_0} = -N_z + \frac{1}{2}(N_x + N_y) \tag{1}$$

$$\eta = \frac{3}{2}\frac{N_x - N_y}{U_p} \tag{2}$$

$$\delta = aN_s + + bN_p \tag{3}$$

where U_p is the p electron imbalance, and $(e^2qQ)_0$ is the electric field gradient corresponding to $U_p = 1$, i.e. $5s^2$ $5p^5$ configuration. $N_{x,y,z}$ are the populations of the $5p_{x,y,z}$ orbitals. N_s and N_p are the populations of 5s and 5p electrons, respectively, and a and b are the proportionality constants.

Although we can not derive the absolute populations from the above equations, we can estimate the change in the electron populations induced by the coordination of the stibines. If the π-back donation is negligible, the change in the value of $(e^2qQ)_{Sb}$, $\Delta(e^2qQ)$, results only from the migration of the $5p_z$ electrons while the populations of $5p_x$ and $5p_y$ orbitals are unchanged. Thus we can estimate the number of the p electrons transferred on the coordination by dividing the value of $\Delta(e^2qQ)$ by that of $(e^2qQ)_0$;

$$\Delta N_p = \frac{\Delta(e^2qQ)}{(e^2qQ)_0} = \frac{(e^2qQ)_{\text{complex}} - (e^2qQ)_{\text{SbR}_3}}{(e^2qQ)_0} \tag{4}$$

where the value of -26 mm s^{-1} is used for $(e^2qQ)_0$ of ^{121}Sb nucleus, being proposed by Parish [8,24]. Once the value of ΔN_p is obtained, we can also estimate the change in N_s, ΔN_s, from the change in the value of isomer shift, $\Delta\delta$, using the following equation,

$$\Delta\delta = \delta_{\text{complex}} - \delta_{\text{SbR}_3} = a\Delta N_s + b\Delta N_p \tag{5}$$

where a and b have the value of -15.0 and 0.80 mm s^{-1} for ^{121}Sb nucleus, respectively, [8,24].

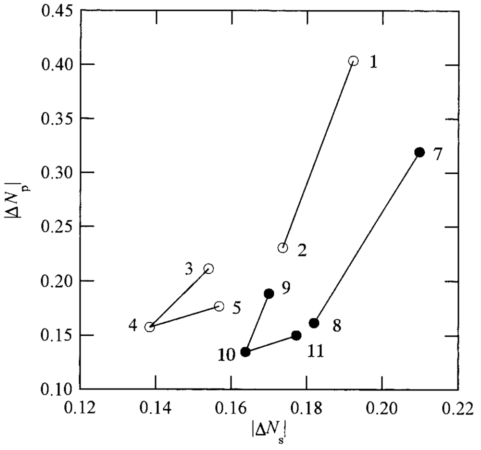


Fig. 4. Relationship between the values of $|\Delta N_s|$ and $|\Delta N_p|$ of $[M(CO)_4(SbMe_3)]$ (open circles) and $[M(CO)_5(SbPh_3)]$ (solid circles). The Arabic numerals in the figure indicate the numbers for the compounds shown in Table 1.

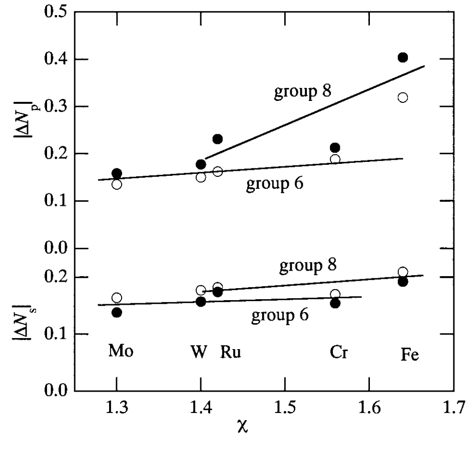


Fig. 5. Relationship between the values of $|\Delta N_s|$ and $|\Delta N_p|$ and Allred–Rochow's electronegativity of the transition metal in $[M(CO)_4(SbMe_3)]$ (open circles) and $[M(CO)_5(SbPh_3)]$ (solid circles).

The obtained values of $|\Delta N_p|$ are plotted against those of $|\Delta N_s|$ in Fig. 4. The values of $|\Delta N_p|$ and $|\Delta N_s|$ are plotted against Allred–Rochow's electronegativity in Fig. 5. The errors in the estimation would be rather large, 0.05 e [8]. $|\Delta N_p|$ has the value of 0.13–0.40 while $|\Delta N_s|$ is 0.14–0.21, and increases as the electronegativity of the transition metal increases. The contribution of 5p electron to M–Sb bond is predominant in iron and $SbMe_3$ complexes. The σ donation of 5p electron is especially strong in the iron complexes, and totally 0.59 and 0.52 electrons are donated to the iron atom in $[Fe(CO_4)(SbMe_3)]$ and $[Fe(CO)_4(SbPh_3)]$, respectively. On the other hand, the σ donation of the 5s electron becomes more important in the $SbPh_3$ derivatives. This indicates that the relative contribution of the 5s and 5p depends on both metal atom and substituent R; the contribution of 5p electrons is more significant in Group 8 complexes and $SbMe_3$ derivatives than the Group 6 complexes and $SbPh_3$ derivatives.

Iron-57 Mössbauer spectra for $[Fe(CO)_4L]$ (L = $SbMe_3$, $SbPh_3$, CO) at 80 K are essentially the same. The values of δ_{Fe} and quadrupole splitting $((\Delta E_Q)_{\text{Fe}}$ are -0.07 and 2.49 mm s^{-1} for $[Fe(CO)_4(SbMe)]$, -0.05 and 2.66 mm s^{-1} for $[Fe(CO)_4(SbPh_3)]$, and -0.08 and 2.52 mm s^{-1} for $[Fe(CO)_5]$, respectively. The value of δ_{Fe} for $[Fe(CO)_4(SbR_3)]$ was slightly larger compared with that of $Fe(CO)_5$. The increase in δ_{Fe} indicates the decrease in the 4s electron density at the Fe nucleus. This is in agreement with the weak σ-donation power of the stibines but the difference is small compared with what would be expected. The values of $(\Delta E_Q)_{\text{Fe}}$ increase in the order $SbMe_3 < CO < SbPh_3$. We cannot explain this order readily but the difference is rather small. Therefore, the coordination of SbR_3 causes little change in the electron distribution around the Fe atom. This implies that some electrons would be re-distributed to maintain the electron density at the iron atom almost constantly since it is hard to believe that SbR_3 has the same σ-donation power as that of CO.

3.2. Seven-coordinate complexes $[MI_2(CO)_3(SbPh_3)L]$ and $[MI_3(CO)_3(SbPh_3)]^-$ (M = Mo, W; L = PPh_3, $AsPh_3$)

Fig. 6 shows the ^{121}Sb Mössbauer spectra for $[MoI_2(CO)_3(SbPh_3)L]$ (L = PPh_3, $AsPh_3$) and $[NBu_4]$ $[MoI_3(CO)_3(SbPh)]$. The spectrum for $[Mo(CO)_5$-$(SbPh_3)]$ is also shown for a comparison. The absorption shapes are more symmetric than those for $[M(CO)_n(SbR_3)]$. The ^{121}Sb Mössbauer parameters are summarized in Table 1.

The Mössbauer spectra show that the σ donation of both 5s and 5p electrons of lone pair is important in M–Sb interactions as in $[M(CO)_5(SbPh)]$. The effect of the acidity of the metal on the Mössbauer parameters found in $[M(CO)_5(SbPh_3)]$ also holds on the neutral

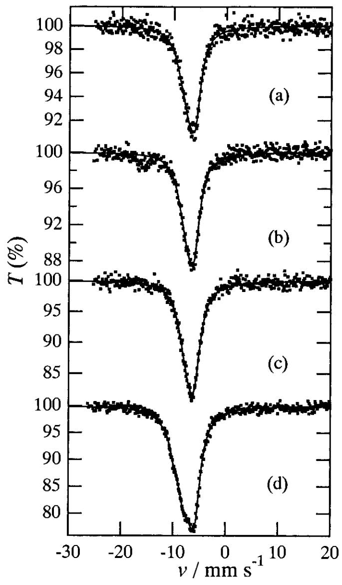
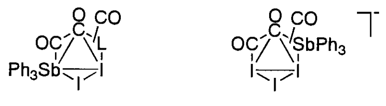


Fig. 6. Sb Mössbauer spectra for the seven- and six-coordinate carbonyl complexes at 20 K (a) $[MoI_2(CO)_3(SbPh_3)(PPh_3)]$, (b) $[MoI_2(CO)_3(SbPh_3)(AsPh_3)]$ (c) $[NBu_4][MoI_3(CO)_3(SbPh_3)]$, (d) $[Mo(CO)_5(SbPh_3)]$.



$[MI_2(CO)_3(SbPh_3)L]$ $[MI_3(CO)_3(SbPh_3)]^-$

Fig. 7. Schematic molecular structure for the seven coordinate complexes.

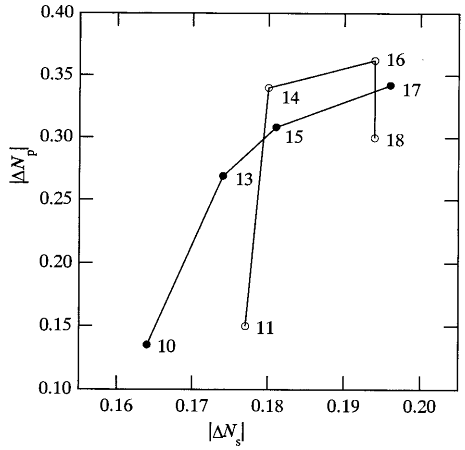


Fig. 8. Relationship between the values of $|\Delta N_s|$ and $|\Delta N_p|$ of $SbPh_3$ derivatives. The Arabic numerals in the figure indicate the numbers for the compounds shown in Table 1.

The values of $(e^2qQ)_{Sb}$ are much smaller than those of the six-coordinate carbonyl complexes, while the values of δ_{Sb} are close to them. Since strong π-back donation for these complexes is unrealistic, the decrease in the value of $(e^2qQ)_{Sb}$ would be related to direct increase in the σ donation of p electrons. One possible explanation for this observation would be the *trans* effect. Carbonyl-capped octahedral structures shown in Fig. 7 have been suggested for $[WI_2(CO)_3(SbPh_3)(PPh_3)]$ and $[NBu_4][WI_3(CO)_3(SbPh_3)]$ based on the low-temperature ^{13}C-NMR spectra and confirmed by an X-ray analysis for $[PPh_2(C_6H_{11})H][WI_3(CO)_3(SbPh_3)]$ [15]. The same configuration would be reasonably expected for other seven-coordinate species though no structural study is reported. According to the speculated structures, $SbPh_3$ is in the *trans* position of PPh_3 or $AsPh_3$ in the neutral complexes and of I in the anionic complexes. $SbPh_3$ is also in *trans* position of the carbonyl in $[M(CO)_5(SbPh_3)]$. The value of $\Delta(e^2qQ)_{Sb}$ decreases in the order $[MI_2(CO)_3(ASPh_3)(SbPh_3)] > [MI_2(CO)_3(PPh_3)(SbPh_3)] \gg [M(CO)_5(SbPh_3)]$ for both Mo and W complexes. This is just the inverse of the strength of the *trans* effect; i.e. $CO \gg PPh_3 > AsPh_3$. The ligand having the strong *trans* effect weakens the bond in the *trans* position. Thus the M–$SbPh_3$ bond is strengthened in the neutral seven-coordinate complexes and consequently the remarkable decrease in $(e^2qQ)_{Sb}$ is observed due to the increase in σ donation of the lone pair. Since the *trans* effect would be smaller for I compared to $SbPh_3$, small values of $(e^2qQ)_{Sb}$ is expected for the anionic seven-coordinate complexes. This expectation holds for Mo complex but not for W complex. The difference in the charge carried in the seven-coordinate complexes; i.e. the values of δ_{Sb} is larger in W complexes, and those of $(e^2qQ)_{Sb}$ is smaller in W complexes than in Mo complexes. However the order of $(e^2qQ)_{Sb}$ is inversed in the anionic complexes, though the difference is small.

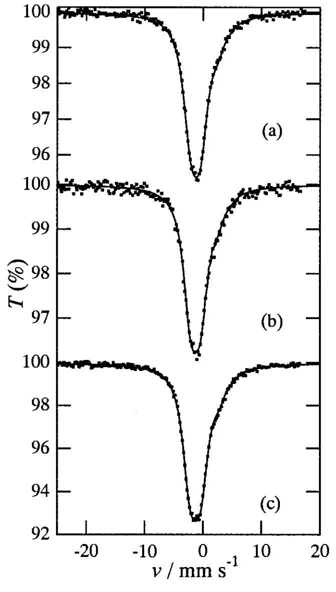


Fig. 9. ^{127}I Mössbauer spectra for seven-coordinate carbonyl complexes at 20 K. (a) $[MoI_2(CO)_3(SbPh_3)(PPh_3)]$, (b) $[MoI_2(CO)_3(SbPh_3)(AsPh_3)]$, (c) $[NBu_4][MoI_3(CO)_3(SbPh_3)]$.

Table 2
^{127}I Mössbauer parameters at 20 K, valence electron populations and charge number on the iodine atom

Compound	δ_I (mm s^{-1}) [a]	($e^2qQ)_I/h$ (mm s^{-1})	($e^2qQ)_I/h$ (MHz)	Γ_{exp} (mm s^{-1})	N_s	N_z	Z_I
$[MoI_2(CO)_3(SbPh_3)(PPh_3)]$	−0.10	−17.9	−829	2.96	1.97	1.64	−0.61
$[WI_2(CO)_3(SbPh_3)(PPh_3)]$	−0.10	−19.3	−896	2.62	1.97	1.61	−0.58
$[MoI_2(CO)_3(SbPh_3)(AsPh_3)]$	−0.10	−17.9	−833	2.84	1.97	1.64	−0.61
$[WI_2(CO)_3(SbPh_3)(AsPh_3)]$	−0.10	−19.0	−881	2.79	1.97	1.62	−0.58
$[NBu_4][MoI_3(CO)_3(SbPh_3)]$	−0.11	−18.9	−879	2.77	1.97	1.62	−0.59
$[NBu_4][WI_3(CO)_3(SbPh_3)]$	−0.08	−18.8	−873	2.87	1.96	1.62	−0.58

[a] Relative to KI at 20 K.

complex might prevent from the simple comparison. The detailed analysis of $|\Delta N_s|$ and $|\Delta N_p|$ shown in Fig. 8 indicates that the *trans* effect operates on both 5s and 5p electrons and that for 5p electron it is much more effective.

The ^{127}I Mössbauer spectra for $[MI_2(CO)_3(SbPh_3)L]$ and $[MI_3(CO)_3(SbPh_3)]^-$ are shown in Fig. 9 and the Mössbauer parameters are listed in Table 2. The asymmetric absorption shape shows that the sign of e^2qQ is negative, indicating that 5p electron density is larger in the xy plane than in the z direction, being the direction of the M–I bond. The ^{127}I parameters are simillar among the complexes, showing that the same electron distribution around the iodine atom.

We can estimate the valence electron populations of the iodine atom from the Mössbauer parameters using Eqs. (1)–(3) [20]. We may assume that N_x and N_y, are 2.0 since the M–I bond would be σ bond, and p_x and p_y orbital scarcely contribute to the M–I bond. The estimated values are also summarized in Table 2 together with the charge on the iodine atom, Z_I. The values for N_s are 1.96–1.97, suggesting that the 5s orbital of iodine atom is almost full-filled and the contribution of iodine 5s electrons to M–I bond is quite small. The values for N_z are 1.61–1.64, implying that 0.36–0.39 electron of iodide ion is withdrawn to the molybdenum and tungsten atom. The number of electrons migrating from the iodide ion is less than those for $SbPh_3$ (0.44–0.55 e) in the same complexes. Neither the kind of the central atom (Mo or W) nor the charge of the complex (neutral or negative) correlate clearly to the number of the migrated electrons in the iodide ion[2]. The number of charges on the iodine atom, Z_I are estimated to be −0.58 to −0.61. This implies that the M–I bond has the considerable ionic character.

A few numbers of the iodine Mössbauer spectra of iodo complexes have been hitherto reported; $[CuI(PPh_3)_3]$ [25], *cis*-$[PtI_2(EPh_3)_2]$ (E = P, As) and $[PtI_2(L–L)]$ (L–L = diphosphine, diarsine) [26]. The values of (e^2qQ), are −470 MHz for $[CuI(PPh_3)_3]$, −1100 to −1220 MHz for *cis*-$[PtI_2(EPh_3)_2]$ and −981 to −1040 MHz for $[PtI_2(L–L)]$. The values of (e^2qQ), for $[MI_2(CO)_3(SbPh)L]$ and $[MI_3(CO)_3(SbPh_3)]^-$ are intermediate of those complexes, suggesting that the M–I interaction in the present complexes is more covalent than that in Cu(I)–phosphine complexes but less in Pt–phosphine complexes.

As a summary, the coordination of stibine ligands to the transition metal atom results in the σ donation of both 5s and $5p_z$ electrons in the lone pair to the transition metal atom for $[M(CO)_n(SbR_3)]$, $[MI_2(CO)_3(SbPh_3)L]$ and $[MI_3(CO)_3(SbPh_3)]^-$. The degree of the σ donation is larger in the Group 8 metals compared to the Group 6 metals. The degree of the σ donation of the 5p electrons has excellent correlation with the values of the Allred–Rochow's electronegativity of the transition metal atoms. The ^{57}Fe Mössbauer spectra suggest that coordination of SbR_3 does not bring about large change in the electron distribution around the Fe atom. The ^{127}I Mössbauer spectra for $[MI_2(CO)_3(SbPh_3)L]$ and $[MI_3(CO)_3(SbPh_3)]^-$ show that the coordination of the iodide ion to the metal atom is a typical σ-bond.

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[2] *Note added in proof*: The smaller N_z values found in the analysis of ^{121}I Mössbauer spectra for W complexes **14** and **16** than the corresponding Mo complexes **13** and **15** may indicate that W withdraws more electrons from I^- through M–I bond than Mo, coinciding with our findings in the analysis of their ^{121}Sb Mössbauer spectra that Mo takes away more electrons in Mo–SbR_3 bond than W does in W–SbR_3 bond in the corresponding complexes.

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