Reaction of Tin Metal Powder with Triorganophosphorus Dihalides: Isolation and Spectroscopic Characterisation of $[PR_3X][SnX_3]$ and *cis*- and *trans*-$Sn(PR_3)_2X_4$ ($X = Br$ or I; $R_3 = Ph_3$, Ph_2Me or $PhMe_2$)

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The novel reaction of some R_3PX_2 compounds ($X = Br$ or I; $R_3 = Ph_3$, Ph_2Me or $PhMe_2$) with unactivated coarse-grain tin metal powder has been investigated. Initially a tin(II) species results which is then further oxidised leading to the formation of both *cis*- and *trans*-$Sn(PR_3)_2X_4$. The products formed have been characterised by elemental analysis, NMR, Raman and Mössbauer spectroscopy and compared to analogous complexes. The synthesis and isolation of the iodo complexes $Sn(PR_3)_2I_4$ by this new synthetic route is straightforward and contrasts with difficulties using conventional techniques, *viz.* the reaction of SnI_4 with PR_3. The relative proportions of *cis*- and *trans*-$SnX_4(PR_3)_2$ isomers formed from the reaction have been determined from Mössbauer spectroscopic studies and the reason for their formation is discussed.

The synthesis of transition-metal complexes by the direct reaction of the metal powder with triorganophosphorus dihalide compounds, R_3PX_2, is now well established. This reaction provides a route not only to known complexes, *e.g.* $[Mn(PR_3)X_2]$[1] and $[PR_3X][Co(PR_3)X_2]$,[2] but also many novel, unexpected compounds, *e.g.* $[Mn_2(PMe_3)_3I_5]\cdot PMe_3$[3] and $[Co(PBu^n_3)_3I_8]$.[4]

More recently we have extended our studies to main group metals, whose co-ordination chemistry with tertiary phosphine ligands has received much less attention than that of transition metals.[5] This new reaction offered an opportunity to prepare previously unknown main group phosphine complexes. These investigations have led to the crystallographic characterisation of the first 1:1 zinc(II) phosphine complex, $[\{Zn(PEt_3)I_2\}_2]$,[6] and, more remarkably, the first phosphine adduct of tin(IV) iodide, *trans*-$Sn(PPr^n_3)_2I_4$.[7] Previous workers have attempted to prepare complexes of the general formula $Sn(PR_3)_2I_4$ and encountered difficulties using the conventional route, *viz.* reaction of anhydrous SnI_4 with tertiary phosphines. Such complexes are readily prepared by the reaction of R_3PI_2 compounds with tin metal, described herein.

The co-ordination chemistry of tin halides with phosphine ligands has received more attention than most main group metals. This almost certainly arises because of the plethora of spectroscopic techniques which can be used to study the resulting complexes. Most studies have concerned the adducts of tin(IV) chloride and bromide.[5] Allison and Mann[8] prepared the complexes $Sn(PR_3)_2X_4$ ($X = Cl$ or Br, $R = Et$ or Pr^n); however, with SnI_4 the adducts were too unstable to be isolated, and until our own recent preparation of $Sn(PPr^n_3)_2I_4$,[7] the only other reports concerning phosphine adducts of SnI_4 are an infrared and Mössbauer spectroscopic investigation of $Sn[PPh(C_6H_4NMe_2\text{-}o)_2]I_4$ and $Sn[o\text{-}(PPh_2)_2C_6H_4]I_4$.[9] In contrast, a number of phosphine adducts of both $SnCl_4$ and $SnBr_4$ have been prepared, and characterised by Mössbauer,[9–13] vibrational[9,14–17] and NMR spectroscopy.[13,18–22] However, only one other complex, *trans*-$Sn(PEt_3)_2Cl_4$, has been crystallographically characterised, by Mather *et al.*[13]

There is a paucity of reports concerning tertiary phosphine complexes of tin(II) halides.[23,24] In an attempt to prepare PBu^t_3 adducts of SnX_4 ($X = Cl$, Br or I) du Mont *et al.*[23] observed that adduct formation did not occur, and instead the tertiary phosphine was oxidised forming a tin(II) phosphonium salt [equation (1)].

$$PBu^t_3 + SnX_4 \longrightarrow [PBu^t_3X][SnX_3] \qquad (1)$$

Herein we report our investigations into the reaction of tin metal powder with a number of R_3PX_2 compounds.

Results

All the compounds reported here were prepared in an identical manner, from the reaction of 2 mol equivalents of the triorganophosphorus dihalide with 1 mol of unactivated, coarse-grain tin metal powder in diethyl ether under argon. Analytical and some spectroscopic data for the compounds are presented in Table 1. The reactions with R_3PBr_2 and $PhMe_2PI_2$ appear to be straightforward, yielding compounds of stoichiometry $Sn(PR_3)_2X_4$, equation (2) ($X = Br$, $R_3 = Ph_3$, Ph_2Me or

$$4R_3PX_2 + 2Sn \xrightarrow{Et_2O,\ ca.\ 5\ d} Sn(PR_3)_2X_4 \qquad (2)$$

$PhMe_2$; $X = I$, $R_3 = PhMe_2$). Subsequent analysis revealed these compounds to be mixtures of both the *cis*- and *trans*-isomers. In contrast, reaction of Ph_3PI_2 or Ph_2MePI_2 with tin produced compounds of slightly different elemental analysis each time the reaction was repeated, typically indicating compounds of formula $Sn_2(PR_3)_3I_8$, equation (3) ($X = I$,

$$4R_3PX_2 + 2Sn \xrightarrow{Et_2O,\ ca.\ 5\ d} [PR_3X][SnX_3] + Sn(PR_3)_2X_4 + R_3P \qquad (3)$$

$R_3 = Ph_3$ or Ph_2Me). Investigations into these compounds revealed them to be mixtures of three products, the tin(II) species $[PR_3I][SnI_3]$ and *cis*- and *trans*-$Sn(PR_3)_2I_4$. The relative proportions of each of these components was different every time the reaction was carried out, thus explaining the slight differences in the elemental analysis of apparently identical products.

^{31}P *NMR Spectroscopic Studies of* $Sn(PR_3)_2X_4$ *and* $Sn_2(PR_3)_3X_8$.—The ^{31}P NMR spectra of all the compounds were recorded in MeCN solution, and all the spectra show two major resonances, Table 1. The resonance located in the region δ 40–60 can be assigned to the presence of the $[PR_3X]^+$ cations in these compounds; similar chemical shifts have been observed for a wide range of $[PR_3I]^+$ species in $CDCl_3$ solution.[25] In several of the compounds this resonance is shifted upfield from the previously observed value of the cation, *e.g.* $[PPhMe_2I]I$ δ 61.9,[25] $[PPhMe_2I][SnI_3]$ δ 48.0. This may be due to solvent effects or to some cation–anion interactions. The other major resonance lies much further upfield, and is tentatively assigned to the tin(IV) species $Sn(PR_3)_2X_4$. For the bromide compounds this assignment can be made with some confidence since values of δ 2.4 and −4.0 have been reported previously for the ^{31}P chemical shifts of $Sn(PEt_3)_2Br_4$[21] and $Sn(PBu^n{}_3)_2Br_4$,[20] respectively. For the iodide compounds the assignment of these peaks to $Sn(PR_3)_2I_4$ compounds is less certain, since no ^{31}P NMR data have been reported for any tertiary phosphine adducts of tin(IV) iodide.

Mössbauer Spectroscopic Studies.—Mössbauer spectroscopic data for all of the compounds are listed in Table 2, and some illustrated in Fig. 1. The data show that in the solid state the iodide complexes are mixtures of three components: *cis*- and *trans*-$Sn(PR_3)_2I_4$ and the tin(II) species $[PR_3I][SnI_3]$. In contrast, the bromide compounds are principally mixtures of *cis*- and *trans*-$Sn(PR_3)_2Br_4$. No $[SnBr_3]^-$ was observed in any of the Mössbauer spectra. The spectra also revealed that several of the products contained a small amount of unreacted tin metal powder (< 12%). The Mössbauer data reported previously for tertiary phosphine adducts of $SnBr_4$ and SnI_4 are presented in Table 3.

Only two of the compounds reported here have previously been studied by Mössbauer spectroscopy, namely *trans*-$Sn(PPhMe_2)_2Br_4$[9] and *cis*-$Sn(PPh_3)_2Br_4$.[10] The data recorded for *trans*-$Sn(PPhMe_2)_2Br_4$ are in agreement with those reported previously.[9] However, the results reported here for *cis*-$Sn(PPh_3)_2Br_4$ are very different to those reported by Philip

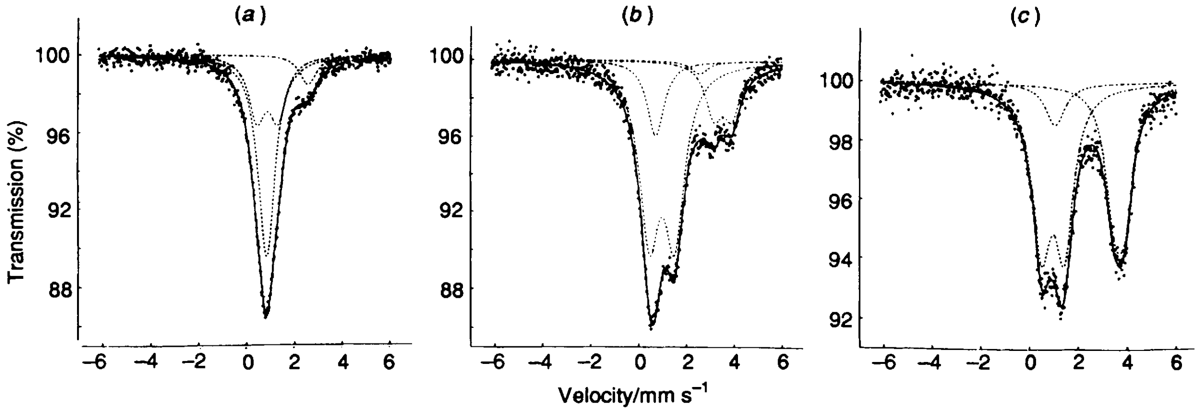


Fig. 1 Mössbauer spectra of the new tin(IV) complexes (*a*) $Sn(PPh_2Me)_2Br_4$, (*b*) $Sn(PPhMe_2)_2Br_4$ and (*c*) $Sn(PPhMe_2)_2I_4$

Table 1 Analytical and spectroscopic data for the $Sn(PR_3)_3I_8$ and $Sn(PR_3)_2X_4$ compounds

		Analysis* (%)			^{31}P-{H} (δ)		
Compound	Colour	C	H	X	$[PR_3X][SnX_3]$	$Sn(PR_3)_2X_4$	$\tilde{\nu}$(Sn–X)/cm^{-1}
$Sn_2(PPh_3)_3I_8$	Brown	32.2 (31.8)	2.2 (2.2)	49.3 (49.8)	49.0	5.0	120
$Sn_2(PPh_2Me)_3I_8$	Brown	25.9 (25.2)	2.2 (2.1)	55.0 (54.8)	59.6	2.3	132
$Sn(PPhMe_2)_2I_4$	Orange	21.6 (21.3)	2.5 (2.4)	55.9 (56.3)	48.0	1.0	128
$Sn(PPh_3)_2Br_4$	Cream	44.5 (44.9)	3.1 (3.1)	33.1 (33.2)	49.9	0.0	180, 202, 226
$Sn(PPh_2Me)_2Br_4$	Cream	35.1 (37.2)	3.0 (2.3)	34.8 (38.1)	45.0	−3.5	182
$Sn(PPhMe_2)_2Br_4$	White	26.8 (26.8)	2.9 (3.1)	44.3 (44.3)	47.0	−4.0	194

* Calculated values in parentheses.

Table 2 Mössbauer parameters[a] for the tin phosphine complexes

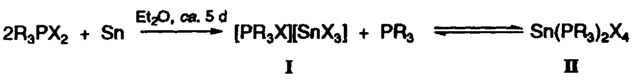
	cis-$Sn(PR_3)_2X_4$				*trans*-$Sn(PR_3)_2X_4$				$[SnX_3]^-$			
Compound	i.s.	q.s.	Γ	%	i.s.	q.s.	Γ	%	i.s.	q.s.	Γ	%
$Sn_2(PPh_3)_3I_8$	1.26	0.00	0.96	61	1.06	1.00	1.01	27	3.88	0.51	0.97	12
$Sn_2(PPh_2Me)_3I_8$[b]	1.24	0.00	0.91	23	1.04	0.84	0.96	35	3.93	0.40	0.89	38
$Sn(PPhMe_2)_2I_4$	1.08	0.00	0.89	4	1.29	0.87	1.02	81	4.01	0.38	0.81	4
$Sn(PPh_3)_2Br_4$[c]	0.80	0.00	0.90	43	0.57	0.99	0.80	45				
$Sn(PPh_2Me)_2Br_4$[d]	0.85	0.00	0.97	55	0.89	0.86	0.91	36				
$Sn(PPhMe_2)_2Br_4$	0.71	0.00	0.44	35	1.03	1.10	1.02	65				

[a] All data recorded at 78 K; i.s. = isomer shift in mm s^{-1}, q.s. = quadrupole splitting in mm s^{-1}, Γ = full width at half height; i.s. values are relative to $CaSnO_3$. Spectra were fitted to singlets and symmetrical doublets. Estimated errors: i.s. 0.03 mm s^{-1}, q.s. 0.06 mm s^{-1}. [b] Also contains β-Sn (4%). [c] Also contains β-Sn (12%). [d] Also contains β-Sn (9%).

Table 3 Reported Mössbauer and $\tilde{\nu}$(Sn–X) vibrational data for tertiary phosphine adducts of tin(IV) bromide and iodide

Compound	Isomer	i.s./ mm s^{-1}	q.s./ mm s^{-1}	$\tilde{\nu}$(Sn–X)/ cm^{-1}	Ref.
$Sn[PPh(C_6H_4NMe_2\text{-}o)_2]I_4$	*cis*	0.84	—	139, 194	9
$Sn[o\text{-}(PPh_2)_2C_6H_4]I_4$	*cis*	1.18	—	167, 182, 205	9
$Sn[PPh(C_6H_4NMe_2\text{-}o)_2]Br_4$	*cis*	0.95	—	203, 216	9
$Sn[o\text{-}(PPh_2)_2C_6H_4]Br_4$	*cis*	1.21	—	208, 220, 234	9
$Sn(PBu^n{}_3)_2Br_4$	*trans*	1.03	1.01	141, 166	10
$Sn[P(C_8H_{17})_3]_2Br_4$	*trans*	0.94	0.89	207	9
$Sn(PPhMe_2)_2Br_4$	*trans*	1.13	1.13	193	9
$Sn(PPh_3)_2Br_4$*	*cis*	0.57	0.66		10

* Mössbauer data suggest oxidation of this species may have occurred, *i.e.* values are in fact for the complex $Sn(OPPh_3)_2Br_4$ (see text).



$$2R_3PX_2 + Sn \xrightarrow{Et_2O,\ ca.\ 5\ d} \underset{\mathbf{I}}{[PR_3X][SnX_3]} + PR_3 \rightleftharpoons \underset{\mathbf{II}}{Sn(PR_3)_2X_4}$$

Scheme 1

et al.,[10] Table 3. The values recorded by these workers are almost identical to those reported by the same workers for *cis*-$Sn(OPPh_3)_2Br_4$ (i.s. = -0.57 mm s^{-1}, q.s. = 0.61 mm s^{-1})[10] a fact noted by Frazer and co-workers[12] who were unable to prepare $Sn(PPh_3)_2Br_4$ as a crystalline solid. Subsequent researchers[9] have recorded the spectrum of $Sn(OPPh_3)_2Br_4$ and obtained identical results, suggesting that Philip *et al.*[10] had oxidised the very air-sensitive $Sn(PPh_3)_2Br_4$ to $Sn(OPPh_3)_2Br_4$. Thus, the values reported here are those of *cis*-$Sn(PPh_3)_2Br_4$. Moreover, the data for this complex fit in well with those of the other *cis*-$Sn(PR_3)_2Br_4$ complexes, Table 3.

The spectra of the iodide complexes contain an additional resonance with an isomer shift that corresponds to a tin(II) species, thus indicating that the $[SnI_3]^-$ anion is present. Previous studies[26,27] have shown that for a given $[SnX_3]^-$ (X = halide) anion, increased anion–cation association results in an increase in the i.s. and a decrease in the q.s. For example in the compounds $[ER_4][SnCl_3]$ when $[ER_4]^+ = [NBu_4]^+$ (non-associated), i.s. = 3.12, q.s. = 1.37; $[AsPh_4]^+$ (slight association), i.s. = 3.28, q.s. = 1.26; $[NEt_4]^+$ (associated), i.s. = 3.43 mm s^{-1}, q.s. = 1.13 mm s^{-1}.[27] The i.s. and q.s. of $[NBu_4][SnI_3]$, which is known to be non-associated in the solid state, are 3.39 mm s^{-1} and 0.79 mm s^{-1}, respectively.[27] These values are significantly different to those reported here for the $[PR_3I][SnI_3]$ compounds, indicating that there is much greater anion–cation interaction in these compounds in the solid state. Moreover, the interaction increases in the order $Ph_3P < Ph_2MeP < PhMe_2P$, suggesting that the degree of association is greater in $[PPhMe_2I][SnI_3]$ than in $[PPh_3I][SnI_3]$.

Despite the comments above concerning trends in i.s. values, the Mössbauer data clearly show the oxidation $Sn^0 \longrightarrow Sn^{II} \longrightarrow Sn^{IV}$, and establish the presence of both *cis*-(singlet) and *trans*-P_2SnX_4 (doublet) components in the final mixture.

Previous workers[9] have noted that there is no systematic trend in i.s. values for pairs of *cis*- and *trans*-$Sn(PR_3)_2X_4$ isomers. In general the i.s. values of *cis* isomers incorporating N- or P-donors are higher than those of the *trans* species, although these differences are small and not diagnostic. Tudela and Rey[28] assigned i.s. values for species SnA_4B_2, based on an analysis of reported Mössbauer data, according to the electronegativities of A and B. For B = P donor, the anticipated i.s. values are 1.02(7) (A = Br) and 1.38(10) mm s^{-1} (A = I). These values correlate reasonably well with the work presented here (Table 2), especially considering the difficulty in deconvoluting overlapping signals which was experienced in our studies. Only one i.s. value looks noticeably anomalous, that of 0.57 mm s^{-1} for *trans*-$Sn(PPh_3)_2Br_4$. This value is close to the range expected for O donors (*i.e.* A = Br, B = O) [0.64(7) mm s^{-1}] and is identical to the value previously reported for *cis*-$Sn(OPPh_3)_2Br_4$, although the larger q.s. value for our compound (0.99 *vs.* 0.66 mm s^{-1}, Table 3) is suggestive of a *trans* stereochemistry, irrespective of the donor atoms. We therefore conclude that for the values reported for '$Sn(PPh_3)_2Br_4$' (Table 3) it cannot be ruled out that oxidation of the PPh_3 has occurred to produce the phosphine oxide complex, $Sn(OPPh_3)_2Br_4$.

Raman Spectroscopy.—According to group theory, for octahedral SnL_2X_4 complexes, four ν(Sn–X) bands are Raman active for the *cis* isomer (idealized C_{2v} symmetry), whereas only two ν(Sn–X) bands are expected for the *trans* isomer (idealized D_{4h} symmetry).[29] This should allow unambiguous structural assignment from the Raman spectrum.

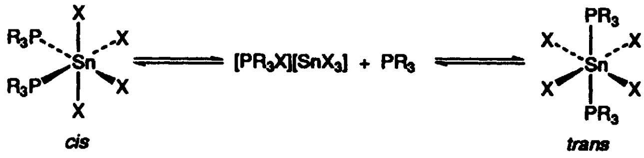
Unfortunately, assignment of the bands in the Raman spectra of the compounds reported here was not straightforward. For the iodide complexes problems arise because the $[SnI_3]^-$ anion also has ν(Sn–I) bands in the same region as the $Sn(PR_3)_2I_4$ species. Moreover, the iodide spectra are of a poor quality due to partial decomposition in the laser beam. Despite these difficulties, for all of the iodide complexes we are able to assign to the single band in the region 120–132 cm^{-1} to the ν(Sn–I) vibration in the *trans*-$Sn(PR_3)_2I_4$ complexes. No other bands could be observed in the spectra of the iodide complexes except for a band at 187 cm^{-1} in the spectrum of $Sn_2(PPh_2Me)_3I_8$ which can be assigned to ν(P–I) in the $[PPhMe_2I]^+$ cation.[25]

The bromide complexes all exhibit a single strong band in the region 180–194 cm^{-1} which is assigned to ν(Sn–Br) in *trans*-$Sn(PR_3)_2Br_4$. The band at 194 cm^{-1} for *trans*-$Sn(PPhMe_2)_2Br_4$ (Table 1) is in good agreement with the value of 193 cm^{-1} reported previously for this compound.[9] The spectrum of $Sn(PPh_3)_2Br_4$ has two much weaker bands at 202 and 226 cm^{-1} which are assigned to ν(Sn–Br) in the *cis* isomer. The spectra of $Sn(PPh_2Me)_2Br_4$ and $Sn(PPhMe_2)_2Br_4$ each contain two additional bands at 145, 167 cm^{-1} and 146, 176 cm^{-1}, respectively. Whilst it seems likely that these bands also result from ν(Sn–Br), their definite origin remains unknown.

Discussion

The reaction of triorganophosphorus dihalides with tin metal powder is clearly very complicated. A possible mechanism for the reaction is given in Scheme 1. The triorganophosphorus dihalide reacts with the tin metal first producing the tin(II) species, **I**, which then undergoes a redox reaction in solution forming the tin(IV) species, **II**. Evidence for this is provided by the ^{31}P NMR spectra, which all contain a resonance which can be assigned to the $[PR_3X]^+$ cation in these compounds, indicative of the tin(II) species $[PR_3X][SnX_3]$. The tin(II) species is even observed in the bromide reactions in solution, there being no evidence for this species in the bromide compounds in the solid state, indicating that the $[PR_3Br][SnBr_3]$ is very unstable, rapidly converting to the tin(IV) species. There has been much interest in *cis–trans* isomerism of octahedral tin(IV) complexes. Usually the compounds exist as either the *cis*- or *trans*-isomer depending on the nature of the ligand or the method of preparation. Nonetheless, for some compounds the existence of both isomers has been detected in solution, by vibrational[30] and NMR[31,32] spectroscopy and in the solid state by vibrational,[30,33] NQR[34] and Mössbauer[35,36] spectroscopy. Very recently *cis–trans* isomerism has been confirmed crystallographically by Tudela *et al.*[36] for $Sn(OPPh_3)_2Br_4$ and by ourselves[7] for $Sn(SMe_2)_2Br_4$. The latter was prepared from the reaction of tin metal with Me_2SBr_2, in an analogous reaction to the work reported here.

Both associative and dissociative mechanisms have been reported for the isomerism in solution in the presence of excess



Scheme 2

ligand,[31,32] whereas for $Sn(OPPh_3)_2Br_4$ isomerisation was controlled thermodynamically.[36]

However, in the reactions reported here, it seems plausible that the isomerism occurs *via* the tin(II) species, Scheme 2, and that oxidation of the tin in $[PR_3X][SnX_3]$ to $Sn(PR_3)_2X_4$ does not favour either the *cis*- or *trans*-isomer, but is entirely random. Evidence for this is provided by previous Mössbauer studies on the products of these reactions, *e.g.* the relative percentages of *cis*- and *trans*-$Sn(PR_3)_2X_4$ in $Sn(PPh_2Me)_2Br_4$ are 55 and 36%, respectively; similarly, for $Sn_2(PPh_3)_3I_8$ the relative percentages of *cis*- and *trans*-$Sn(PPh_3)_2I_4$ and $[PPh_3I][SnI_3]$ are 61, 27 and 12%, respectively, but in an identical reaction the relative percentages were 30, 40 and 30%. The redox behaviour of tertiary phosphine adducts of SnX_4 ($X = Cl$, Br or I) is not without precedent. du Mont *et al.*[23] reported that when PBu^t_3 was treated with SnX_4, oxidation of the phosphine, forming $[PBu^t_3X][SnX_3]$ occurred, rather than adduct formation.

The reaction of tin with triorganophosphorus dihalides is both interesting and complex, resulting in the formation of a tin(II) species which then undergoes further reaction leading to the simultaneous formation of both *cis*- and *trans*-$Sn(PR_3)_2X_4$. Furthermore, and in contrast to the findings of previous workers who could not isolate $Sn(PR_3)_2I_4$ complexes using conventional synthetic techniques, *viz.* the reaction of anhydrous SnI_4 with tertiary phosphines, the synthesis of these compounds by the reaction of R_3PI_2 with tin metal powder is an entirely straightforward process, again illustrating the utility of this new synthetic route for the synthesis of new metal complexes.

Experimental

All the compounds reported here are air- and moisture-sensitive, some intensely so. All manipulations of starting materials and products were carried out in a Vacuum Atmospheres HE493 glove-box under a dry argon atmosphere. Diethyl ether was distilled over CaH_2 and subsequently sodium wire prior to use. A typical reaction is outlined below.

The compound $PhMe_2PI_2$ (0.5 g, 1.27 mmol) and tin metal powder (BDH) were added to freshly distilled diethyl ether (50 cm^3) in a reaction vessel fitted with a Rotaflo stopcock. The reactants were then allowed to stir for *ca.* 5 d at room temperature, after which the resultant orange solid was isolated using standard Schlenk techniques. The solid was dried *in vacuo*, and stored in pre-dried, argon-filled ampoules.

Elemental analyses were carried out by the UMIST Microanalytical Service. The $^{31}P-\{^1H\}$ NMR spectra were recorded on a Bruker AC200 NMR spectrometer; all shifts are reported relative to 85% concentrated phosphoric acid standard.

Raman spectra were recorded at the University of Manchester Service using a Coherent Innova 90 argon-ion laser and a SPEX 1403 0.85 m focal length double monochromator fitted with a BCGS microscope attachment. The radiation was detected using a Hammamatsu R928 photomultiplier tube, cooled to -30 °C using a Products for Research Inc. TE177 RF-005 cooler housing.

Mössbauer spectra were recorded at 78 K on a constant acceleration spectrometer (Cryophysics Ltd.) fitted with a room temperature 10 mCi $CaSnO_3$ source. Details of the experimental procedure are given elsewhere.[37]

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