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Note

The reaction of diiodotriorganophosphorus compounds with dicobalt octacarbonyl; isolation of a new isomeric form of $[R_3PI][CoI_3(PR_3)]$

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Abstract

The novel reaction of R_3PI_2 compounds with dicobalt octacarbonyl has been investigated and compared to previous studies involving the reaction of R_3PI_2 compounds with cobalt metal powders. The products produced from both reactions have identical stoichiometries but, surprisingly, possess different structures. Infrared and Raman spectroscopic studies and X-ray powder diffraction clearly show that the products obtained from the reaction of R_3PI_2 with $Co_2(CO)_8$ are a new isomeric form of $[R_3PI][CoI_3(PR_3)]$, compared to the products isolated from the reaction of R_3PI_2 with cobalt metal powder. Seven examples of this new isomeric form of $[R_3PI][CoI_3(PR_3)]$ are reported and have been characterised by elemental analysis, Raman and quantitative electronic spectroscopy and magnetic data, the latter indicating that some antiferromagnetic coupling occurs. Some general investigations into the reaction mechanism for these reactions are reported and discussed.

Keywords: Cobalt complexes; Organophosphorus complexes; Dihalogenotriorganophosphorus compounds

1. Introduction

The accepted method of synthesis of tertiary phosphine complexes of transition metals in their common oxidation states is the reaction of a transition metal salt with the tertiary phosphine ligand in some stoichiometric ratio. Since a metal salt can be viewed as an oxidised metal, we wondered if, instead, an oxidised tertiary phosphine, R_3PX_2 (X = Br, I), could be reacted with an unoxidised metal to produce tertiary phosphine complexes, (Eq. (1)).

$$\mathbf{M} + \mathbf{n}\mathbf{R}_{3}\mathbf{P}\mathbf{X}_{2} \rightarrow \mathbf{M}(\mathbf{P}\mathbf{R}_{3})_{n}\mathbf{X}_{m} + \mathbf{X}_{n-m}$$
(1)

It has now been demonstrated that this novel synthetic method not only produces known metal complexes [1] (i.e. those produced by conventional synthesis), novel isomers of existing complexes [2], complexes of metals in mixed oxidation states [3], complexes of metals in recognised high oxidation states [4], complexes with non-predictable geometry [5], and complexes not thought capable of existence, e.g. the penta-coordinated cobalt(III) complex $CoI_3(SbPh_3)_2$ [6], a species the existence of which contravenes the SHAB rule.

The metal powder reagents used in this new synthetic method are unactivated, i.e. crude, off-the shelf metals, presumably covered with an oxide coating. Thus, we recognise that the R_3PX_2 species must be powerful oxidising reagents. We therefore have begun to examine the reactivity of these R_3EX_2 (E=P, As, Sb) oxidants towards other zerovalent metal species, e.g. Ph_3AsI_2 reacts with $Co_2(CO)_8$ in a 6:1 molar ratio to produce [$(Ph_3AsI)_2I$][$CoI_3(AsPh_3)$], a complex which contains the first crystallographically characterised cobalt(II)-tertiary arsine bond in the tetrahedral [$CoI_3(AsPh_3)$]⁻ anion and the novel cation which contains the linear Ph_3As-I-I-I-AsPh_3 array [7].

Because of these interesting results [7], we have further investigated the use of $Co_2(CO)_8$ as a metal(O) reagent in reactions with R_3PI_2 species, having previously examined cobalt metal powder as the metal reagent: thus, cobalt powder [8] reacts with a large number of diiodotertiaryphosphine compounds (Eq. (2)).

$$2R_3PI_2 + Co \rightarrow [R_3PI][CoI_3(PR_3)]$$
⁽²⁾

 $(R_3 = Et_3, Pr^n_3, Bu^n_3, PhMe_2, Ph_2Me, Ph_2Pr^n, Ph_3 (o-, m-, p-CH_3C_6H_4)Ph_2, (m-CH_3C_6H_4)_3)$

Because of the interesting and wide variety of species formed by reaction of cobalt powder with R_3PI_2 , e.g. $[Bu^n_3PI)_2(\mu-I)][(Bu^n_3PI)(\mu-I)CoI_3]$ [9], and because of the promising results from the $Co_2(CO)_8$ reaction with Ph₃AsI₂ [7], we have investigated the reaction of $Co_2(CO)_8$ with a number of R_3PI_2 ligands, in order to compare these results with those obtained from the reaction of crude cobalt metal with R_3PI_2 species [8].

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2. Results and discussion

All of the complexes described here were prepared by a similar route, that is, the R_3PI_2 compound ($R_3 = Ph_3$, Me_3Ph , Et₃, Pr^n_3 , (*p*-FC₆H₄)₃, (*p*-CH₃OC₆H₄)₃, (*p*-CH₃SC₆H₄)-Ph₂] was added to dicobalt octacarbonyl in a 4:1 molar ratio in diethyl ether under strictly anhydrous and anaerobic conditions (Eq. (3)). The reaction in each case led to the removal of all carbon monoxide ligands from the metal, as observed by the absence of ν (C–O) modes in the IR spectra of the bulk solids.

$$\operatorname{Co}_{2}(\operatorname{CO})_{8} + 4\operatorname{R}_{3}\operatorname{PI}_{2} \xrightarrow{\operatorname{N}_{2}, \mathrm{r.t.}, 3-5 \text{ days}} 2\operatorname{CoI}_{4}(\operatorname{PR}_{3})_{2} + 8\operatorname{CO} \quad (3)$$

Elemental analyses for these complexes are shown in Table 1. The electronic spectra of all the complexes were recorded in dichloromethane solution; the spectrum of each complex consists of three or four bands at 790–680 nm, some of which are seen as shoulders. The spectra recorded in Table 2, are typical for tetrahedral cobalt(II) species and give molar extinction coefficients of around 400–700 mol⁻¹ dm³ cm⁻¹, which are also typical for this type of complex.

Magnetic susceptibilities of each of the complexes were recorded at room temperature, Table 2, and for all the complexes, except for $R_3P = (p-FC_6H_4)_3P$ and $(p-CH_3SC_6H_4)Ph_2P$, fall in the region 3.8–4.2 $\mu\beta$. This is slightly lower than the values usually observed for tetrahedral cobalt(II) complexes [10], and suggests antiferromagnetic

Table 1

Analytical data for [R₃PI] [Co(R₃P)I₃] complexes

coupling between adjacent cobalt(II) ions. This lowering of μ_{eff} is not observed for $[(p-CH_3SC_6H_4)_3PI][CoI_3\{(p-CH_3SC_6H_4)_3P\}]$ and this may be due to the more sterically demanding thioanisyl group, preventing close interaction between adjacent cobalt centres.

Although the materials produced from the reaction of cobalt metal powder [8] have the same stoichiometry as those produced from $Co_2(CO)_8$, i.e. $CoI_4(R_3P)_2$, the structures produced via the latter route are not the same as the $[R_3PI][CoI_3(PR_3)]$ complexes produced from cobalt metal. A comparison of the X-ray powder diffraction patterns of the complexes of stoichiometry Co(Ph₃P)₂I₄, Fig. 1, shows that their structures are quite different. Moreover, a study of the solid state Raman spectra, Fig. 2, also shows differences between the products derived from the two routes. The complexes $[R_3PI][CoI_3(R_3P)]$, prepared from cobalt powder, show a strong $\nu(P-I)$ band in the low frequency Raman spectrum at a similar wavenumber to that of the corresponding R₃PI₂ ligand [8]. For the complexes prepared in this work from dicobalt octacarbonyl, however, the ν (P–I) band, Table 1, is shifted to a higher energy by as much as 22 cm^{-1} , thus indicating that the complex formed has a much stronger P-I bond.

The different properties exhibited by the complexes formed on reaction of dicobalt octacarbonyl with triorganophosphorus diiodides, compared with those of the established complexes prepared from cobalt metal powder, poses a number of important questions. (i) What is the structure of the complex prepared from the metal carbonyl, proposed to have

Complex	Colour	Elemental analyses: (calc.)found (%)			Raman bands
		с	Н	I	ν(P-1) (cm ⁻⁺)
[Ph ₃ PI][Co(Ph ₃ P)I ₃]	bright green	(39.6)39.5	(2.7)2.5	(46.6)46.4	187
$[Me_2PhPI][Co(Me_2PhP)I_3]$	dark green (tar)	(22.8)22.7	(2.6)2.6	(60.3)59.8	
$[Et_3PI][Co(Et_3P)I_3]$	bright green	(17.9)18.8	(3.7)3.3	(63.3)60.9	243
$[Pr^{n}_{3}PI][Co(Pr^{n}_{3}P)I_{3}]$	bright green	(24.4)22.7	(4.7)4.6	(57.3)60.9	
$[(p-FC_{6}H_{4})_{3}PI][Co{(p-FC_{6}H_{4})_{3}P}I_{3}]$	mid green	(37.8)37.5	(2.1)2.4	(44.4)44.9	168
$[Ph_2(p-CH_3SC_6H_4)_3PI][Co{(p-CH_3OC_6H_4)_3P}I_3]$	dark green	(38.5)38.5	(2.9)3.1	(42.9)43.0	168
$[p-CH_3OC_6H_4)_3PI][Co{[p-CH_3OC_6H_4)_3P}I_3]$	light green	(39.7)40.8	(3.3)3.1	(40.0)38.0	

Table 2

UV-Vis band maxima for $[R_3PI][Co(R_3P)I_3]$ complexes in dichloromethane solution

Complex	λ (nm) (ϵ_{max} dm ³ mol ⁻¹)	$ \begin{aligned} \lambda \ (nm) & \lambda_2 \ (nm) \\ (\epsilon_{max} \ dm^3 \ mol^{-1}) & (\epsilon_{max} \ dm^3 \ mol^{-1}) \end{aligned} $		$\lambda_4 (nm)$ ($\epsilon_{max} dm^3 mol^{-1}$)	$\mu_{ m eff}/\mueta$	
[Ph ₃ PI][Co(Ph ₃ P)I ₃]	781.0(970)		709.0(636)	693.5(627)	4.2	
$[Me_2PhPI][Co(Me_2PhP)I_3]$	781.0(663)	– (sh)	728.5(449)	701.5(418)	4.1	
$[Et_3PI][Co(Et_3P)I_3]$	778.5(49.3)	756.0(529)	728.0(455)	699.0(41.4)	4.2	
$[Pr^{n}_{3}PI][Co(Pr^{n}_{3}P)I_{3}]$	788.0(781)	– (sh)	729.5(456)	699.0(315)	4.1	
$[(p-FC_{6}H_{4})_{3}PI][Co{(p-FC_{6}H_{4})_{3}P}I_{3}]$		759.0(421)	720.5(399)	694.0(341)	3.8	
$[Ph_2(p-CH_3SC_6H_4)_3PI][Co{Ph_2(p-CH_3SC_6H_4)_3P}I_3]$		745.5(496)	719.0(516)	693.5(434	4.9	
$[p-CH_3OC_6H_4)_3PI][Co{(p-CH_3OC_6H_4)_3P}I_3]$	772.5(301)		715.5(368)	684.5(301)(sh)	4.0	



Fig. 1. The X-ray powder diffraction patterns of $[Ph_3PI][Co(PPh_3)I_3]$ prepared from (a) cobalt metal powder and (b) dicobalt octacarbonyl.



Fig. 2. The Raman spectra of $[Ph_3PI][Col_3(PPh_3)]$ prepared from (a) cobalt metal powder and (b) dicobalt octacarbonyl.

the ionic stoichiometry, $[R_3PI][CoI_3(R_3P)]?$ (ii) Is it possible to prepare the same species using both starting materials, i.e. dicobalt octacarbonyl or cobalt metal powder, if the reaction conditions are varied, and hence, does an equilibrium exist between the two species? (iii) Can the new complexes be prepared only from the reaction of $Co_2(CO)_8$ with R_3PI_2 , or can they be prepared from $Co_2(CO)_8$, R_3P and I_2 , i.e. is the initial preparation of the triorganophosphorus diiodide essential to the reaction? In order to address these questions we decided to concentrate upon the reactions of Ph_3PI_2 with dicobalt octacarbonyl and coarse grain cobalt metal powder as representative examples.

A comparison of the products of the reactions of Ph₃PI₂ with cobalt metal powder and with dicobalt octacarbonyl at various temperatures from 20-60 °C was made. For the metal powder reaction the same product was consistently formed, as identified by the X-ray powder diffraction patterns. The product from the reaction with dicobalt octacarbonyl also remained the same until the temperature of the reaction was raised above 40 °C, when a solid of variable stoichiometry was obtained. It is probable that at these temperatures the thermal decomposition of Co₂(CO)₈ occurs at a greater rate than does its reaction with Ph₃PI₂, thus leading to a mixture of reaction products. None of the reaction conditions employed, however, yielded the same products for both starting materials. The two reaction routes consistently led to the formation of the two respective reaction products. Thus, the 'unknown' complex formed from dicobalt octacarbonyl cannot be prepared from the metal powder.

As previously described, a comparison of the Raman spectra of the two complexes shows a substantial strengthening of the P-I bond in the unknown structure. This is supported by a comparison of the IR spectra of these complexes with that of Ph₃PI₂, given in Table 3. Studies by Jensen and Nielson [11], and Kross and Fassel [12], have shown that certain areas of the IR spectrum of tertiary aryl phosphines are sensitive to the electronegativity at the phosphorus atom. In particular a phenyl-related vibration at ~1050–1125 cm⁻¹ and the C₃P asymmetric modes at ~490-540 cm⁻¹ experience variations in both frequency and intensity upon change in the electronegativity at the phosphorus centre. In comparing these areas of the spectrum for Ph₃PI₂ and the two Co(Ph₃P)₂I₄ complexes prepared by different reaction routes it is clear that a change at the phosphorus centre does occur, Table 3.

The IR spectra of Ph_3PI_2 and the product of the metal powder reaction are very similar and show very little change in electronegativity at the phosphorus centre. However, the spectrum of the product of the carbonyl reaction shows a shift in the so-called 'x-sensitive' band at 1099.5 to 1101.5 cm⁻¹ accompanied by a significant reduction in intensity. The bands in the 480–540 cm⁻¹ region are also shifted and show varied intensity compared to the product of the metal powder reaction, Table 3. This implies an increase in electronegativity at the phosphorus centre which would well be due to the increased strength of the P–I bond.

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Compound	IR stretches					
Ph ₃ I ₂	1121.7(w)	1099.5(vs)	1024.3(w)	995.4(s)		
	540.1(w,br)	516.99(vs)	505.4(s)	497.7(vs)		
[Ph ₃ PI][CoI ₃ (PPh ₃)] prepared from cobalt	1122.7(w)	1097.6(vs)	1028.2(w)	995.4(s)		
	540.1(w,br.)	516.99(vs)	505.4(s)	497.7(vs)		
[Ph ₃ PI][CoI ₃ (PPh ₃)] prepared from Co ₂ (CO) ₈	1145.9(s)	1122.7(s)	1101.5(s)	1028.2		
	544.0(s)	538.2(s)	518.9(vs)	997.3(s)		
	· ·			490.0(s)		

Furthermore, it should be noted that the high ν (P–I) band observed in the Raman spectrum of the Co(Ph₃P)₂I₄ complex derived from the metal carbonyl complex is not unique. An identical Raman spectrum has been reported by McAuliffe and co-workers [5] for the zinc complex of the same stoichiometry, Zn(Ph₃P)₂I₄, derived from the reaction of zinc metal powder with triphenylphosphine diiodine, Fig. 3. The structure of this complex is not known, but is seems likely that this complex has the same structure as the unknown cobalt complex prepared here. It is interesting to note that no variation in the band frequencies is seen between the zinc and cobalt complexes, thus implying that these bands are not directly associated with the metal centres. Unequivocal identification of the structure is, however, not possible from the information reported here. All attempts to grow crystals of



Fig. 3. The Raman spectra of (a) $[Ph_3PI][CoI_3(PPh_3)]$ prepared from dicobalt octacarbonyl and (b) $[Ph_3PI][ZnI_3(PPh_3)]$ prepared from zinc metal powder.

these complexes suitable for single crystal X-ray diffraction studies have so far been unsuccessful.

In order to demonstrate that initial preparation of the diiodophosphorane is essential to the reactions described here a series of 'one-pot' and two step reactions were carried out, reactions (4-6):

$$\operatorname{Co}_{2}(\operatorname{CO})_{8} + 4\operatorname{Ph}_{3}\operatorname{P} + 4\operatorname{I}_{2} \xrightarrow{\operatorname{Et}_{2}\operatorname{O}}$$

$$\overset{\operatorname{Et}_{2}\operatorname{O}}{\overset{\operatorname{H}_{2}}{\longrightarrow}}$$

$$(4)$$

$$\operatorname{Co}_2(\operatorname{CO})_8 + 4\operatorname{Ph}_3\operatorname{P} \longrightarrow \operatorname{product} \text{ isolated} \longrightarrow$$
 (5)

$$Co_2(CO)_8 + 4I_2 \xrightarrow{H_2O} \text{ product isolated} \xrightarrow{4 \mu n_3 \mu}$$
 (6)

For each of the above reactions a green solid was isolated. Elemental analyses for the bulk products were different in each case and could not be fitted to any exact stoichiometries. The 'one-pot' reaction proceeded via a yellow intermediate which we believe is Ph_3PI_2 . It is possible that a mixture of reactions occurred here, including the reaction of triphenyl-phosphine with dicobalt octacarbonyl; the reaction of diiod-ine with dicobalt octacarbonyl and the formation of triphenylphosphine diiodine and its subsequent reaction with dicobalt octacarbonyl. The IR spectrum of the isolated mixture showed weak ν (C–O) bands at 2013.9 and 1994 cm⁻¹, indicating that some carbon monoxide-containing material remained.

The two-step reaction (5), resulted initially in the formation of a red-brown solid proposed to be $[Co(CO)_3(Ph_3P)]_2$ from the first step of the reaction. Subsequent addition of diiodine to the reaction mixture resulted in vigorous effervescence, indicating the rapid removal of carbon monoxide ligands. The IR spectrum of the bulk product once more, however, showed $\nu(C-O)$ bands at 1994.7 and 1944 cm⁻¹; the solid product is again thought to be a mixture.

Reaction of $Co_2(CO)_8$ with diiodine has been reported to cause decomposition of the carbonyl complex, leading to a mixture of unidentified products [13]. Addition of triphenylphosphine to the dark brown solution obtained from this reaction in diethyl ether, led to the formation of a yellow solid, proposed to be Ph₃PI₂. The colour of the reaction mixture gradually became green with stirring for 24 h. The IR spectrum of the product showed that the carbon monoxide ligands had indeed all been removed. However, no single product could be identified from this reaction. In conclusion, therefore, it is believed that the unknown complex, proposed to be an isomeric form of the ionic complex $[Ph_3PI][CoI_3(Ph_3P)]$, can only be prepared in good yield, by the reaction of dicobalt octacarbonyl with Ph_3PI_2 at temperatures below 40 °C. The subtlety of reaction of the novel oxidising agents, R_3PI_2 and the great variety of products available from their reaction with various metal(O) reagents is thus clearly indicated.

3. Experimental

All the cobalt complexes described are moisture sensitive therefore strictly anaerobic and anhydrous conditions were adhered to during their synthesis. The synthesis of the R_3PI_2 compounds has been described elsewhere [13] and the R_3PBr_2 compounds were synthesised in an analogous manner. Diethyl ether was obtained from BDH, dried over sodium wire for ~1 day and then distilled over CaH₂ in an inert atmosphere prior to use; it was distilled directly into the reaction vessel and degassed with nitrogen sparge. Standard reagent-grade coarse-grain cobalt metal powder obtained from Aldrich was used as received. After isolation, any subsequent manipulation of the complexes was carried out inside a Vacuum Atmospheres HE-493 glove-box.

The same reaction technique was employed in the synthesis of all the complexes in order to establish a reactivity pattern. The synthesis of $[Et_3PI][Co(Et_3P)I_3]$ is typical. Triethylphosphine diiodide (0.831 g, 2.23 mmol) was suspended in diethyl ether (~100 cm³) and subsequently dicobalt octacarbonyl (0.191 g, 0.56 mmol) was added. After ~2 days the resultant bright green solid formed was isolated by standard Schlenk techniques and dried in vacuo. It was then transferred to pre-dried argon-filled ampoules which were subsequently flame sealed. Yields for all the complexes were essentially quantitative.

Elemental analyses (Table 1) were performed by the analytical laboratory of this department. Electronic spectra were recorded on a Shimadzu UV-2101PC spectrophotometer. IR spectra were recorded on a Nicolet 5PC FTIR spectrometer. Raman spectra were recorded by the University of Manchester Raman service using a Coherent Innova 90 5W argon-ion laser and a SPEC 1403 double monochromator (focal length 0.85 m) fitted with a BGCS microscope sampling attachment. The radiation was detected using a Hamamatsu R928 photomultiplier tube which was cooled to -30 °C in a Products for Research Inc. TE 177 RF-005 cooler housing. The data were processed on a SPEX DM1B data station. X-ray powder diffraction patterns were recorded using a Scintag XRD2000 powder diffractometer using Cu K α radiation of $\lambda = 1.5418$ Å. Magnetic susceptibilities were recorded using a Oxford Instruments CF 12000 Faraday balance.

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