

The Use of the Novel Oxidising Reagent Triphenylarsine Diiodine in the Reaction with Dicobalt Octacarbonyl to produce a New Type of Complex $[(\text{Ph}_3\text{AsI})_2\text{I}][\text{Co}(\text{AsPh}_3)_3]$

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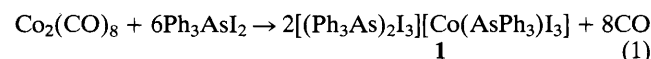
Ph_3AsI_2 oxidises $\text{Co}_2(\text{CO})_8$ in a 6 : 1 molar ratio to produce the novel complex $[(\text{Ph}_3\text{AsI})_2\text{I}][\text{Co}(\text{AsPh}_3)_3]$ in quantitative yield, the first crystallographically characterised complex containing a cobalt(II)-tertiary arsine bond and the unusual linear cation $[\text{Ph}_3\text{As-I-I-AsPh}_3]^+$.

We have reported recently the novel reaction of triorganophosphorus dihalogen compounds, R_3PX_2 , with unactivated coarse grain metal powders to produce a variety of metal phosphine complexes.¹⁻⁵ We have established that this new reaction scheme produces unconventional complexes containing the metal in an unusually high oxidation state, e.g. $\text{Ni}(\text{PMe}_3)_2\text{I}_3$,¹ novel isomers of existing complexes, e.g. $\text{Mn}(\text{PPhMe}_2)_2\text{I}_2$,¹ as well as previously unknown complexes, e.g. $[\text{Mn}_2(\text{PMe}_3)_3\text{I}_5] \cdot \text{PMe}_3$ and $[(\text{Bu}^n_3\text{PI})_2(\mu\text{-I})][\text{Bu}^n_3\text{PI}(\mu\text{-I})\text{CoI}_3]$ ² and complexes of non-predicable geometry, e.g. $[\{\text{Zn}(\text{PEt}_3)_2\}]_2$.³ The subtlety of this new reaction route has been illustrated in previous studies with manganese metal powder, where the reaction with Ar_3PI_2 ($\text{Ar} = \text{Ph}$, substituted aryl) yields monomeric $\text{Mn}(\text{PAr}_3)_2\text{I}_2$ and MnI_2 , whereas with reaction with R_3PX_2 ($\text{R}_3 =$ trialkyl, mixed alkyl/aryl; $\text{X} = \text{Br}$, I) yields polymeric $\text{Mn}(\text{PR}_3)_2\text{X}_2$.⁴

Clearly, the reaction of metal powders with triorganophosphorus dihalogen compounds is a fruitful new synthetic method to a wide range of metal phosphine complexes. However, in discussing our results thus far, we have placed

most emphasis on the surprising reactivity of coarse-grain metal powders, contrasting this with the much more experimentally limiting previous methods of employing metals as reagents in synthetic inorganic chemistry, viz. metal vapours,^{6,7} dispersed metals⁸ and the electrolytic reaction of cathodic metals.⁹ However, probably the key factor in this new chemistry is the discovery of the powerful oxidising ability of the R_3PX_2 reagents. Hence, we have embarked on a study of the reaction of this type of reagent with acknowledged metal-containing complex species as the starting materials. Here, we report the reaction of $\text{Co}_2(\text{CO})_8$ with Ph_3AsI_2 to yield the novel $[(\text{Ph}_3\text{AsI})_2\text{I}][\text{Co}(\text{AsPh}_3)_3]$.

Dicobalt octacarbonyl reacts quantitatively with Ph_3AsI_2 in a 1 : 6 molar ratio under anhydrous and anaerobic conditions to produce a green solid, quantitatively, in ca. 5 days, see eqn. (1).



Complex **1** was recrystallised from dry diethyl ether to yield dark-green crystals† suitable for single crystal X-ray determination. The crystal structure‡ of **1** is illustrated in Fig. 1. This unusual complex contains two discrete fragments. The first consists of the extraordinary cation $[(\text{Ph}_3\text{AsI})_2\text{I}]^+$, which contains two Ph_3AsI units linked by an iodine bridge; the $\text{Ph}_3\text{As-I-I-AsPh}_3$ cation is completely linear. This contrasts vividly with the non-linear (I-I-I , 101.2°) array in $[(\text{Bu}^n_3\text{P})_2\text{I}_3]^+$,² and this further illustrates the subtlety of this synthetic procedure. Moreover, the $d(\text{As-I})$ bonds in the cation of **1** [2.508(5), 2.554(5) Å] are distinctly different and are both slightly shorter than the $d(\text{As-I})$ of $\text{Ph}_3\text{As-I-I}$ [2.64(1) Å];¹⁰ moreover the $d(\text{I-I})$ bonds are lengthened [3.194(5), 3.235(5) Å] compared with 3.005(1) Å in Ph_3AsI_2 .¹¹ The I-I distances in $[(\text{Ph}_3\text{AsI})_2]^+$ are also considerably shorter than in the non-linear cation $[(\text{Bu}^n_3\text{PI})_2\text{I}]$ [3.42(1), 3.62(1) Å].² The reasons for the differences in the nature of these two cations is probably that the linear arrangement As-I-I-As is in agreement with a $26e^-$ bonding system, while the 'V' shaped P-I-I-P is in accordance with a $24e^-$ system. The

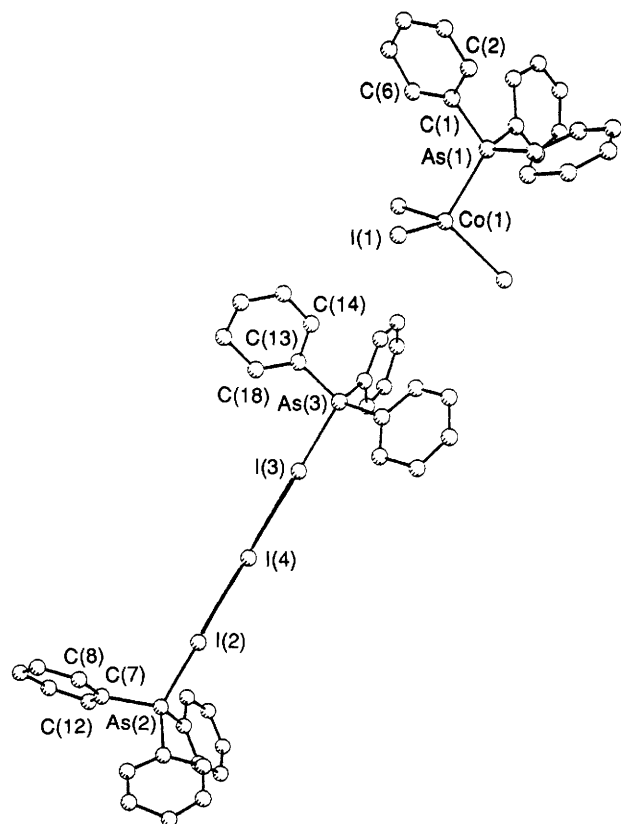


Fig. 1 Selected bond lengths (Å) and angles ($^\circ$) in $[(\text{Ph}_3\text{AsI})_2\text{I}][\text{Co}(\text{AsPh}_3)_3]$ I(1)–Co(1) 2.575(3); As(1)–Co(1) 2.519(8); As(1)–C(1) 1.91(3); I(3)–As(3) 2.554(3); As(3)–C(13) 1.87(3); I(2)–As(2) 2.508(5); As(2)–C(7) 1.98(2); Co(1)–As(1)–C(1) 114.8(9); C(1)–As(1)–C(1) 104(1); I(1)–Co(1)–I(1) 113.5(1); I(1)–Co(1)–As(1) 105.1(2); As(1)–C(1)–C(2) 119(2); I(3)–As(3)–C(13) 107.0(7); As(3)–C(13)–C(14) 121(2); I(2)–As(2)–C(7) 112.5(6); C(7)–As(2)–C(7) 106.2(7); As(2)–C(7)–C(8) 115(2)

† Complex **1** has been characterised by satisfactory elemental analysis (C,H,I), decomp. 156.9°C , VIS spectroscopy: 1.1×10^{-3} mol dm^{-3} solution in diethyl ether gave two bands, $\lambda = 621.1$ and 674.5 nm ($\epsilon_{\text{max}} = 899$ mol $^{-1}$ dm^3 dm^{-1}) and Raman spectroscopy: bands observed at 173 cm^{-1} , $\nu_{\text{Co-I}}$, 347 cm^{-1} , $\nu_{\text{Co-As}}$, bands were also observed at 242 and 313 cm^{-1} attributable to Ph_3As . The low frequency Raman spectrum of Ph_3AsI_2 was recorded for comparative purposes and gave bands at 122 cm^{-1} , $\nu_{\text{As-I}}$ and 99 cm^{-1} , $\nu_{\text{I-I}}$.

‡ Crystal data for $[(\text{Ph}_3\text{AsI})_2\text{I}][\text{Ph}_3\text{AsCoI}_3]$: $M_r = 1739.07$, rhombohedral, space group $R3c(h)$ (no. 161), $a = 13.513(4)$, $c = 54.65(1)$ Å, $V = 8642(4)$ Å 3 , $Z = 6$, $D_c = 2.005$ Mg m^{-3} , Mo-K α radiation ($\lambda = 0.71069$ Å), crystal dimensions $0.4 \times 0.4 \times 0.2$ mm 3 , 3671 reflections were collected on a Rigaku AFC6S diffractometer yielding 969 observed [$I > 3.00\sigma(I)$]. The structure was solved by direct methods and refined by full-matrix least-squares analysis (TEXSAN) to a final $R = 0.044$, $R_w = 0.056$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

difference in the nature of these cations is, therefore, probably due to the higher electronegativity of phosphorus compared with arsenic.

The second fragment is the $[\text{Co}(\text{AsPh}_3)\text{I}_3]^-$ anion which represents the first crystallographically characterised complex containing a cobalt(II)-arsine bond. Although numerous cobalt(0)-arsine complexes are known,¹¹⁻¹³ those containing cobalt in a higher oxidation state are much rarer¹⁴⁻¹⁶ and no X-ray structural information is available.

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