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# Facile Synthesis of a Mononuclear Palladium(II) Hydride Stabilized by Tri-tert-butylarsine and its Conversion into a Hydridobridged Dinuclear Palladium(II) Hydride

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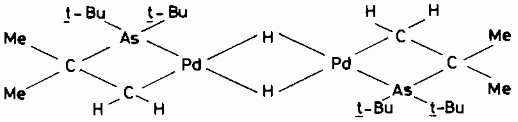
Since the first report [1] on stable palladium(II) hydrides, only a few such compounds have been prepared. The compounds are of the type, *trans*-$PdHXL_2$ (L = a bulky phosphine and X = halide or other anionic ligand), and satisfactory methods for their preparation have been found only recently. These include either the reduction [2] of a palladium(II) salt with sodium borohydride in the presence of phosphine or oxidative addition [3, 4] of protic acids, HX, to the bis(tertiary phosphine) palladium(0) complexes, $PdL_2$. Although stable platinum(II) dihydrides as well as hydridobridged dinuclear platinum(II) complexes have been reported [5] recently, analogous palladium(II) compounds are not known.

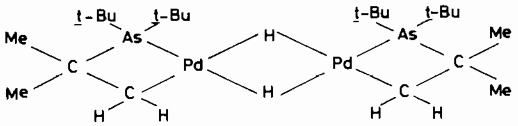
In the course of our investigations on the reactions of palladium(II) with tri-tert-butylarsine we have discovered a very convenient synthetic route for the preparation of a new stable hydride, $PdHCl[As(t\text{-}Bu)_3]_2$, (*1*), which can be readily converted into a hitherto unknown type hydridobridged dinuclear palladium(II) hydride, (*2*). The preparation of (*1*) involves the conversion of a Pd–Cl bond into a Pd–H bond by alcohol which has not been observed before. The reported work also provides the first example of the stabilization of palladium(II) hydrides by arsenic ligands.

Reaction of commercially available $Na_2PdCl_4$ and tri-tert-butylarsine in absolute alcohol at room temperature, affords the air-stable yellow $PdHCl[As(t\text{-}Bu)_3]_2$, (*1*), in over 60% yield. The formulation of the product is confirmed by analytical, infrared and $^1H$ NMR spectral data. Its infrared spectrum (Nujol mull) shows strong bands at 2157 and 752 $cm^{-1}$ due to the Pd–H stretching and bending frequencies, respectively. Its $^1H$ NMR spectrum (in $C_6D_6$) consists of a single peak ($\delta$ = 1.50 ppm) in the *t*-butyl region and another single peak in the region upfield from TMS ($\delta$ = –18.06 ppm). A *trans* structure can be assigned to (*1*) by comparing its Pd–H stretching frequency and the upfield proton resonance with those for *trans*-$PdHCl[P(t\text{-}Bu)_3]_2$ [3, 4]. The observation of a single resonance due to the two $As(t\text{-}Bu)_3$ ligands is also indicative of a *trans* structure.

Solid *trans*-$PdHCl[As(t\text{-}Bu)_3]_2$ is stable at room temperature for several months. However, upon dissolving in benzene it slowly undergoes intramolecular condensation to give the metalated hydridobridged dinuclear palladium(II) complex, (*2*); the conversion is complete within three days.



(2) trans



(2) cis

The formulation of (*2*) is supported by the analytical and $^1H$ NMR spectral data. Its $^1H$ NMR spectrum (in $C_6D_6$) shows three peaks in the t-butyl region at $\delta$ 1.22 ($CH_2$), 1.46 ($CMe_2$) and 1.28 $\{As(t\text{-}Bu)_2\}$ ppm, in the ratio 1:3:9, and a single resonance at $\delta$ = –4.31 ppm. The signals at 1.46 and 1.28 ppm are indicated to be doublets suggesting the presence of both *cis* and *trans* isomers.

The phosphine complexes, *trans*-$PdHX[P(t\text{-}Bu)_3]_2$, are reported [4] to undergo rapid intramolecular metalation. However, in marked contrast with the conversion of (*1*) into (*2*), the metalation in the phosphine complexes results in the cleavage of the Pd–H bond. Further work on the reactivity of palladium(II) hydrides stabilized by tri-*tert*-butylarsine is in progress.

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