The Synthesis of [Diphenyl(*N*-*p*-tolyl)phosphinimidoyl]bis(diphenylthiophosphinoyl)methane, Its Stabilized Anion and a Coordination Complex of Rhodium(I)†

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The title compound was synthesized by the reaction of $[Ph_2P][Ph_2P(S)]_2CH$ with *p*-tolyl azide; its resonance-stabilized anion and a coordination complex, $Rh(cod)\{[Ph_2P(S)]_2[Ph_2PN(p\text{-}tol)C]$ (cod = cycloocta-1,5-diene), of the anion were also synthesized and characterized.

Since the synthesis of $[Ph_2P(S)]_3CH$, $HtrisS_3$,‡ by Issleib and Abicht in 1970,[1] a large number of analogues $HtrisX_3$, where X's are different combinations of the chalcogens O, S and Se have been reported.[2] Abstraction of the acidic methine hydrogen of $HtrisX_3$ by methoxide anion has generated a set of uninegative, potentially tridentate ligands which can coordinate *via* the chalcogens in both a bidentate[3] and tridentate[4] fashion to create a host of new coordination complexes.

We report here a new member of this series of ligands which has a P=NR functionality (R = *p*-tolyl) and thereby adds nitrogen to the existing list of chalcogens as a potential donor atom. This compound, $HtrisS_2NR$ **1**, was synthesized by the direct reaction of $[Ph_2P(S)]_2[Ph_2P]CH$ with *p*-tolyl azide[5,6] and isolated as a moisture-sensitive off-white solid in >95% yield. The $^{31}P\{^1H\}$ NMR spectrum of **1** has the expected doublet and triplet resonances at δ 43.0 for the phosphine sulphide and δ 36.6 for the phosphine imide, respectively with two-bond P–P coupling of 29.0 Hz. The chemical shift of the phosphine sulphide is normal[2] while the phosphine imide's chemical shift is considerably downfield in comparison to that of other previously reported phosphine imides $Ph_3P{=}NR$, where R is *p*-tolyl (δ 2.97[7]), Ph (δ 3.0,[8] 3.3)[7] and $SiMe_3$ (−1.8).[8] The phosphine imide chemical shift in **1** is more akin to those of aminophosphonium salts, *e.g.* $[Ph_3PNHPh]Br$, δ 32.0.[8] Furthermore the methine proton resonance of **1**, expected to be a double triplet at about δ 5.6–6.3,[2] is not observed in that range. The proton 'missing' from the methine carbon, however, is observed at 213 K as a doublet at δ 10.18 with $^2J_{P\text{-}H}$ 19.1 Hz. Selective decoupling of the imine phosphorus resonance collapses this doublet to a singlet. We conclude that the phosphine imide nitrogen is sufficiently

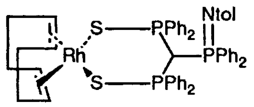
$HtrisS_2NR$ **1** $trisS_2NR^-$ **2**

$Rh(cod)(trisS_2NR)$ **3**

R = *p*-MeC_6H_4

[†] For Part 15 of the series Polydentate Ligands Including Phosphorus, see ref. 13.

[‡] $HtrisS_3$ = $[Ph_2P(S)]_3CH$; $HtrisS_2N(p\text{-}tolyl)$ = $[Ph_2P(S)]_2[Ph_2PN(p\text{-}tolyl)]CH$, *etc.*



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basic [*cf.*, the pK_b of the $Ph_3P{=}N(p\text{-tolyl})$ is 6.1[6]] intramolecularly to abstract the acidic hydrogen from the methine carbon to form a mesomerically stabilized zwitterion with structures B, C and D. The tautomer A does not appear to exist under these conditions. The proton resonances at ambient temperature of the amino protons in quaternary phosphonium salts, which might be somewhat similar in electronic environment to the *N*-proton in **1**, are reported to be broad peaks at δ 7.3 for $[Ph_3PNH_2]Cl$[9] or obscured by the phenyl protons in some analogues[10] of the latter compound. In contrast, the *N*-proton resonance in free $Ph_3P{=}NH$ is a doublet at δ 1.61 and in the complex $Mo_2(CO)_6(\mu\text{-}Ph_3PNH)_3$ it appears as a doublet at δ 0.52, $^2J_{P-H}$ 12 Hz.[11]

Abstraction of the *N*-hydrogen from **1** was achieved with lithium diisopropylamide and the resulting anion, $trisS_2NR^-$ **2**, was isolated as the lithium salt, a slightly air-sensitive and very moisture-sensitive tan solid. The $^{31}P\{^1H\}$ NMR spectrum of **2** consists of a doublet at δ 44.8 for the phosphine sulphide and a triplet at δ 32.8 for the phosphine imide with $^2J_{P-P}$ 22.6 Hz. The downfield resonance of the imino hydrogen of **1** at 213 K is not evident in **2**.

Reaction of **2** with $[Rh(cod)Cl]_2$ yielded a dark-gold product $Rh(cod)(trisS_2NR)$ **3**. The $^{31}P\{^1H\}$ NMR spectrum of **3** consists of a doublet for the phosphine sulphide at δ 36.7 and a triplet for the phosphine imide at δ 8.9 with $^2J_{P-P}$ 26.9 Hz. The upfield coordination shift of the phosphine sulphide is of the same magnitude as those observed in other Rh(cod)-$(trisX_3)$ complexes.[12] The large upfield chemical shift for the phosphine imide phosphorus is consistent with its non-coordinated nature and is in the range cited for other previously reported non-coordinated phosphine imides.[8] The ^{31}P NMR data of **3** therefore are consistent with square-planar geometry about Rh^I with the $trisS_2NR$ ligand coordinated in a bidentate fashion *via* both sulphurs while the phosphine imide nitrogen remains non-coordinated as shown in structure E. Further coordination chemistry of this ligand is being investigated.

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