

Synthesis, properties, and some rhodium, iridium, and platinum complexes of a series of bulky *m*-terphenylphosphine ligands



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ABSTRACT

A series of sterically demanding aryl phosphine ligands (**L**) bearing terphenyl substituents, $\text{PR}_2\text{Ar}'$ ($\text{R} = \text{hydrocarbyl}$, $\text{Ar}' = 2,6\text{-diarylphenyl radical}$) has been prepared and characterized. The stability of these ligands towards oxidation in the air has been tested, and theoretical and experimental studies aimed to provide information on their electronic and steric properties have been performed. Treatment of the metal dimers $[\text{MCl}(\text{COD})]_2$ ($\text{M} = \text{Rh}$, Ir ; $\text{COD} = 1,5\text{-cyclooctadiene}$) with ligands $\text{PMe}_2\text{Ar}^{\text{Xyl}_2}$ (**L1**) and $\text{PMe}_2\text{Ar}^{\text{Dipp}_2}$ (**L5**), in a 1:1 metal:ligand ratio, afforded the expected square-planar 16-electron complexes $[\text{MCl}(\text{COD})(\text{PMe}_2\text{Ar}^{\text{Xyl}_2})]$ and $[\text{MCl}(\text{COD})(\text{PMe}_2\text{Ar}^{\text{Dipp}_2})]$, respectively. These compounds were readily converted into the corresponding dicarbonyl derivatives, $[\text{MCl}(\text{CO})_2(\text{PMe}_2\text{Ar}^{\text{Xyl}_2})]$ and $[\text{MCl}(\text{CO})_2(\text{PMe}_2\text{Ar}^{\text{Dipp}_2})]$, respectively. While the expected $\kappa^1\text{-P}$ coordination mode of the $\text{PR}_2\text{Ar}'$ ligands is found for these rhodium and iridium species, the mononuclear $\text{Pt}(\text{II})$ derivative obtained by reaction of PtCl_2 with $\text{PMe}_2\text{Ar}^{\text{Dipp}_2}$ has composition $[\text{PtCl}_2(\text{PMe}_2\text{Ar}^{\text{Dipp}_2})]$, and exhibits a bidentate $\kappa^1\text{-P}$, $\eta^1\text{-arene}$ coordination mode involving one of the *ipso* carbon atoms of a flanking terphenyl aryl ring. The corresponding carbonyl compound $[\text{PtCl}_2(\text{CO})(\text{PMe}_2\text{Ar}^{\text{Dipp}_2})]$, was generated under a CO atmosphere and exhibits $\kappa^1\text{-P}$ coordination mode.

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1. Introduction

Phosphines and related phosphorus-donor Lewis bases are one of the most widely used classes of ligands in homogenous catalysis, coordination and organometallic chemistry [1]. Their electronic and steric features can easily be modified in systematic and predictable ways [2], allowing for the design of metal complexes with specific characteristics with regard to red-ox behaviour, solubility, electrophilicity, and other properties. In particular, the use of sterically demanding phosphines, either in their monodentate or polydentate versions, permits kinetic stabilization of low-coordinate organometallic complexes and agostic structures [3], unusual geometries [4], highly reactive metal–carbon bonds [5], etc. In this context, it is worth mentioning the crucial role of a bulky pincer-type diphosphonite ligand (PONOP) in the characterization of the first σ -methane complex reported by Brookhart et al. in 2009 [6].

In recent years, bulky phosphines have promoted challenging metal-catalyzed transformations leading to the synthesis of high

value products, as witnessed by outstanding contributions from the groups of Beller [7], Buchwald [8], Fu [9], and Hartwig [10], among others. As a prominent example, Buchwald-type heteroleptic dialkylbiaryl phosphines PR_2Ar ($\text{Ar} = \text{biphenyl}$) have found wide application in palladium catalyzed cross-coupling and carbon–heteroatom bond formation [11]. Although these ligands are nowadays commercially available for an ample range of biaryl (Ar) substituents, only a restricted set of bulky alkyl R groups, mainly $t\text{Bu}$ (CMe_3) and Cy (C_6H_{11}), has been introduced in their molecular structures. It has been proposed that the high activity of catalytic systems that combine metal complexes with dialkylbiaryl phosphines is often to ascribe to the ability of the biaryl group to bind to the metal centre through weak so-called secondary interactions [11b], thus stabilizing coordinatively unsaturated reaction intermediates. In consequence, similar to other aryl phosphines, biaryl- and terphenylphosphines may be viewed as hemilabile ligands [12] by virtue of $\eta^1\text{-arene}$ coordination of a pendant aryl ring.

In spite of the enormous popularity of biarylphosphines within the chemical community, information on the analogous terphenylphosphines, $\text{PR}_2\text{Ar}'$ ($\text{Ar}' = \text{terphenyl group}$) is rather

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scarce and limited to a handful of ligands and a few coordination complexes with late transition metals [3k,13]. It is, however, noteworthy that the exceptional protecting steric features of bulky terphenyl groups permitted in 2005 the isolation of the first quintuply bonded dimetal complex by Power and collaborators [14]. Our research group has recently employed these large organic radicals to generate unusual quadruply bonded dimolybdenum complexes [15], and some terphenylphosphines to stabilize low coordinate Pt(0) species [3k], and cationic digold complexes [13e]. In this contribution, we describe the synthesis and characterization of a family of bulky dialkyl terphenylphosphine ligands, together with the study of their air-stability and of some examples of coordination compounds of late transition metals. DFT calculations and experimental work have also been employed to estimate the steric bulk of these ligands and their electron-donating features.

2. Results and discussion

2.1. Synthesis and spectroscopy

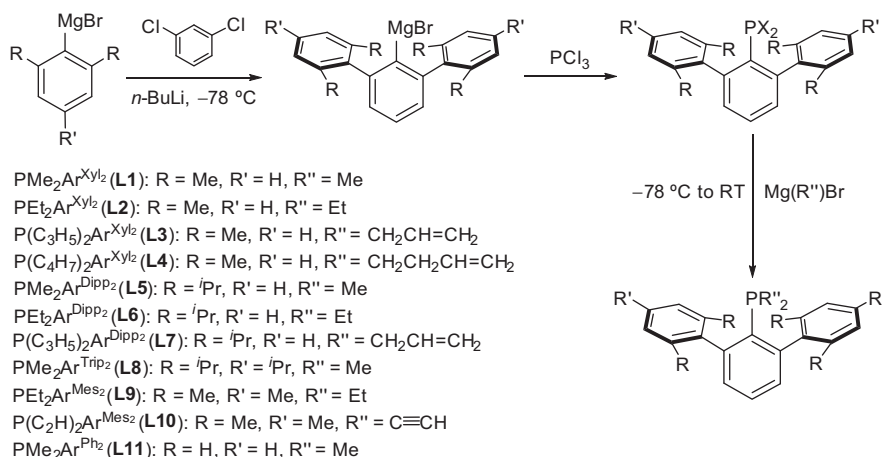
Ligands **L1–L11** were prepared analogously to ligands **L1** and **L5**, whose synthesis has recently been reported by our group [3k,13d]. Ordered from the least to the most steric demanding, we employed the following terphenyl groups: 2,6-diphenylphenyl (Ar^{Ph_2}), 2,6-bis(2,6-dimethylphenyl)phenyl (Ar^{Xyl_2}), 2,6-bis(2,4,6-trimethylphenyl)phenyl (Ar^{Mes_2}) [13a–c], 2,6-bis(2,6-di(isopropyl)phenyl)phenyl ($\text{Ar}^{\text{Dipp}_2}$), and 2,6-bis(2,4,6-tri(isopropyl)phenyl)phenyl ($\text{Ar}^{\text{Tipp}_2}$). The procedure we propose is essentially based on that reported by Protasiewicz and collaborators [13a] but employs a terphenyl Grignard reagent instead of the analogous terphenyl lithium compound, as the source of the terphenyl fragment (Scheme 1). Moreover, the last step of the synthesis, that is the transformation of dihalo terphenylphosphines into the corresponding dihydrocarbyl terphenylphosphines, was also performed with the use of Grignard reagents in all cases. Ligands **L1–L11** were isolated in moderate to high yields (based on Mg(Ar')Br) as fairly air-stable colourless solids. It is noteworthy that the synthetic procedure can start directly from the dihalo terphenylphosphines, $\text{Ar}'\text{PX}_2$, which were prepared in a large scale (up to 8 g approximately), isolated as moisture-sensitive solid mixtures of $\text{Ar}'\text{PCl}_2$, $\text{Ar}'\text{PClBr}$, and $\text{Ar}'\text{PBr}_2$, and stored under a nitrogen or an argon atmosphere.

Compounds **L1–L11** feature high solubility in common aprotic organic solvents such as dichloromethane, chloroform, ethers,

toluene, and pentane, even at low temperatures. On the other hand, they exhibit scarce solubility in cold methanol, which was the solvent of choice for their purification. Single crystals of phosphines **L7** and **L10** were grown by slow evaporation of concentrated pentane solutions and analyzed by X-ray diffraction analyses. Their molecular structures in the solid state are depicted in Fig. 1. By analogy with the structures reported for other *m*-terphenylphosphines [13b,l], the PR_2 unit is bent away from one of the lateral rings of the terphenyl substituent. This distortion reduces steric interactions and results in P–C–C angles that differ significantly. Thus, in $\text{P}(\text{C}_3\text{H}_5)_2\text{Ar}^{\text{Dipp}_2}$, **L7**, the P1–C6–C5 and P1–C6–C7 angles are of 114.1(1) and 127.2(1)°, respectively, while in $\text{P}(\text{C}_2\text{H}_5)_2\text{Ar}^{\text{Mes}_2}$, **L10**, the corresponding angles have values 111.6(2) and 128.6(2)°. The bond distances from the phosphorus atom to the carbon atoms of the hydrocarbyl substituents in **L7** are very similar (1.860(2) and 1.856(2) Å, for P1–C31 and P1–C34, respectively). They become somewhat different in the bis(acetylide) phosphine **L10**, where the P1a–C24 bond to the acetylide oriented towards the mesityl group is slightly elongated (1.792(4) Å) relative to the P1a–C26 bond that points to the empty space between the mesityl rings (1.770(3) Å). Probably to relieve the steric hindrance, the acetylide group above the mesityl ring (C24–C25) distorts appreciably at C24, with a C25–C24–P1a angle of 163.5(2)°, vs. 172.2(3)° for C26–C26–P1a.

All of the newly reported $\text{PR}_2\text{Ar}'$ ligands were fully characterized by elemental analysis and multinuclear NMR spectroscopy. Their solution ^1H NMR spectra are consistent with a high degree of apparent symmetry as a result of fast rotation around the $\text{C}_{\text{aryl}}\text{—C}_{\text{aryl}}$ or P– $\text{C}_{\text{Ar}'}$ bonds (Scheme 2).

$^{31}\text{P}\{^1\text{H}\}$ NMR studies revealed that the phosphorus nucleus of ligands **L1–L11** resonates in an ample frequency range, with chemical shift in the interval from –74.3 to –8.3 ppm (Table 1). It has long been known [16] that the phosphorus substituents have an additive effect on the ^{31}P NMR shift, with deviations in the predicted δ values usually smaller than 5–6 ppm. [16c] The four dimethylterphenylphosphines studied in this work, namely **L1** (Ar^{Xyl_2}), **L5** ($\text{Ar}^{\text{Dipp}_2}$), **L8** ($\text{Ar}^{\text{Tipp}_2}$), and **L11** (Ar^{Ph_2}) feature $\delta(^{31}\text{P})$ in the narrow range from –41.3 to –35.6 ppm. These δ values are close to the contribution of the two P–Me substituents (–21 ppm each [16c]), albeit of somewhat smaller absolute magnitude. Ethyl substituents offer a smaller contribution of roughly –7 ppm each, whereas longer chain *n*-alkyl radicals have intermediate contributions of about –11 ppm. [16c] Thus, it is not unexpected that the $\text{PEt}_2\text{Ar}'$ ligands **L2** (Ar^{Xyl_2}), **L6** ($\text{Ar}^{\text{Dipp}_2}$), and **L9** (Ar^{Mes_2}) resonate in the vicinity of –9 ppm, while the bis(allyl) and



Scheme 1. Synthesis of ligands **L1–L11**.

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