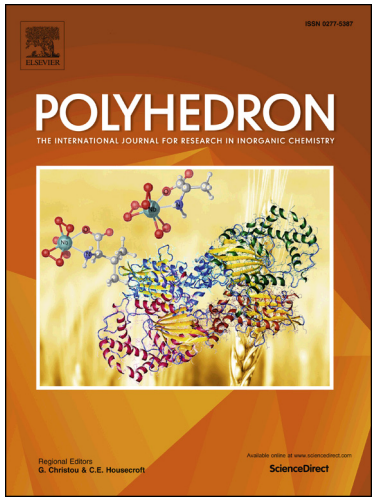

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Heteroleptic Nickel Complexes of a Bulky Bis(carbene)borate Ligand

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Abstract

Bis(carbene)borate ligand transfer to the nickel nitrosyl synthon $Ni(NO)(PPh_3)_2Br$ provides the new nickel nitrosyl complex $Ph_2B(^tBuIm)_2Ni(NO)(PPh_3)$. The solid state structure reveals a trigonal pyramidal nickel ion with a very long bond to the apical PPh_3 ligand. The complex reversibly dissociates PPh_3 in solution to afford three-coordinate $Ph_2B(^tBuIm)_2Ni(NO)$, with NMR data providing evidence for PPh_3 binding at low temperatures. Ligand transfer to $Ni(PMe_3)_2Cl_2$ provides the square planar complex, $Ph_2B(^tBuIm)_2Ni(PMe_3)Cl$, which shows no evidence for rearranging to the form a homoleptic complex with two bis(carbene)borate ligands. This complex is a suitable synthon for the $[Ph_2B(^tBuIm)_2Ni]^+$ fragment, as demonstrated by the synthesis of the π-allyl complex $Ph_2B(^tBuIm)_2Ni(\eta^3\text{-}C_7H_7)$. The π-allyl complex reacts with O_2 to provide benzaldehyde and an unstable complex that is tentatively identified as the nickel(II) hydroxide $[Ph_2B(^tBuIm)_2Ni(\mu\text{-}OH)]_2$.

Keywords

Nickel complexes; nitrosyl ligands, NHC complexes, bidentate ligands; dioxygen reactivity

Introduction

Among his many scientific contributions, Bill Jones has elegantly demonstrated the utility of strongly donating bulky ligands in nickel chemistry. For example, the Ni(dippe) fragment (dippe = $^iPr_2PCH_2CH_2PiPr_2$) is notable for its involvement in organonitrile C-CN bond cleavage [1] as well as thiophene and benzothiophene desulfurization.[2] Moreover, using this same fragment, Bill's group foreshadowed a new era in metal-ligand multiple bonds[3] by providing some of the first evidence for a terminal metal-ligand multiple bond involving a late 3d transition metal, in the form of a transient nickel sulfide.[4]

The strong σ-donor nature and synthetic flexibility of *N*-heterocyclic carbenes (NHC) have driven the development of these ligands well beyond their initial application as phosphine surrogates. Although the utility of nickel complexes with monodentate NHCs is relatively well established,[5] nickel complexes with bidentate bis(carbene) donor ligands are still relatively rare.[6,7,8,9] Despite this limited body of work, the application of bidentate bis(carbene) nickel complexes in metal-ligand multiple bond chemistry[8e] and C-C