2-Pyridylbis(diphenylphosphino)methane chemistry. Synthesis and structures of \([\text{Cu}(\mu-\eta^2:\eta^1-(\text{Ph}_2\text{P})_2\text{-CHC}_5\text{H}_4\text{N})(\text{THF})]_2(\text{BF}_4)_2\) and \([\text{Ni}(\text{Ph}_2\text{PCH}_2\text{C}_5\text{H}_4\text{N})_2][\text{NiCl}_4]\cdot0.85\text{CH}_2\text{Cl}_2\)

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Reaction of 2-pyridylbis(diphenylphosphino)methane (NPP) with \([\text{Cu}(\text{NCMe})_4]\text{BF}_4\) and with \([\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2\) forms \([\text{Cu}(\text{NPP})(\text{THF})]_2(\text{BF}_4)_2\) (after recrystallization in the presence of THF) (1) and \(\text{NiCl}_2(\text{NPP})\) (2) respectively. Attempts to recrystallize 2 led ultimately to the ligand cleavage product \([\text{Ni}(\text{Ph}_2\text{PCH}_2\text{C}_5\text{H}_4\text{N})_2][\text{NiCl}_4]\cdot0.85\text{CH}_2\text{Cl}_2\) (3). Complex 1 crystallizes in the monoclinic space group \(P2_1/n\) with \(a = 13.148(2)\), \(b = 19.221(2)\), \(c = 13.458(2)\) \(\text{Å}\), \(\beta = 108.61(1)\), \(V = 3222.6(8)\) \(\text{Å}^3\), \(Z = 2\). The structure was refined on \(F^2\) to \(R1 = 0.11\), \(wR2 = 0.14\) for 5661 observed reflections. Complex 3 crystallizes in the triclinic space group \(P1\) with \(a = 12.795(2)\), \(b = 17.535(1)\), \(c = 10.203(1)\) \(\text{Å}\), \(\alpha = 107.564(6)\), \(\beta = 114.260(8)\), \(\gamma = 78.435(8)\), \(V = 1982.1(8)\) \(\text{Å}^3\), \(Z = 2\). The structure was refined on \(F\) to \(R1 = 0.044\), \(wR = 0.059\) for 3534 observed reflections. Dinuclear complex 1 has crystallographically imposed centrosymmetry with the NPP ligands arranged in a head-to-tail fashion. The Cu...Cu separation of 3.372(1) \(\text{Å}\) is too long to support significant metal–metal interaction. Complex 3 results from the cleavage of a \([\text{PPH}_2]\) unit from the NPP ligand and contains an approximately square planar nickel atom surrounded by two Ph₂PCH₂C₅H₄N ligands coordinated in a head-to-head fashion.

KEY WORDS: Copper; dinuclear; nickel; cationic complex; P–N ligand.

Introduction

Bidentate ligands containing the P–N donor set such as Ph₂PCH₂CH₂NMe₂ and Ph₂PCH₂C₅H₄N are termed “hemilabile” because the nitrogen donor is frequently more weakly coordinated to a metal than is the phosphorous donor which often permits facile opening of the chelate ring without total loss of the ligand. These and related ligands have been employed in mechanistic studies of the chelate ring opening reactions of metal carbonyl complexes\(^\text{1,2}\) and to provide “lightly stabilized” complexes for use in catalytic applications.\(^\text{3–5}\) Extension of these ideas to dinuclear complexes suggests that 2-pyridylbis(diphenylphosphino)methane (NPP; \(I (X=\text{H})\)) would be a suitable hemilabile ligand and, indeed, a number of homodinuclear and heterobimetallic complexes in which the pyridyl nitrogen can be readily displaced from the metal have been reported.\(^\text{6–10}\) In addition, a number of mononuclear complexes of \(I (\text{NPP} (X=\text{Me}))\) in which both N–P and P–P coordination modes were proposed without structural confirmation have been prepared.\(^\text{11}\) As part of our continuing studies on dinuclear complexes we have undertaken a fuller investigation of the ligand properties of NPP and report here on some initial results.

Experimental

All reactions were carried out under prepurified nitrogen using standard Schlenk techniques and sol-
vents which were purified by standard methods and distilled under nitrogen. Proton and $^{31}\text{P}[^1\text{H}]$ NMR spectra were obtained on an IBM/Bruker AF200 spectrometer at 200.132 and 81.015 MHz, respectively, with chemical shifts referred to external tetramethylsilane and 85% phosphoric acid, respectively. Published methods were used to prepare $\text{[Cu(}\mu$-$\eta^3$-$\eta^1$-$\{(\text{C}_6\text{H}_5)p\}_2\text{CHC}_6\text{H}_4\text{N}\}$(C$_4$H$_8$O)$_2$)$_2$·(BF$_4$)$_2$ (1).

To a dichloromethane solution (10 mL) of 0.20 g (0.64 mmol) of $\text{[Cu(NCMe)}_4\text{]}$BF$_4$ was added 0.29 g (0.64 mmol) of NPP dissolved in 5 mL of the same solvent. After several minutes of stirring at room temperature a white powder began to precipitate. The precipitation was completed by addition of diethyl ether and the product was filtered off, washed with diethyl ether and dried in vacuo. Recrystallization by layering a nitromethane solution of the crude product with tetrahydrofuran afforded glistening colorless crystals in ca. 80% yield. Anal. Calcd for C$_{68}$H$_{66}$B$_2$Cu$_2$F$_2$N$_2$O$_2$P$_4$: C, 59.71; H, 4.87; N, 2.05%. Found: C, 59.5; H, 4.9; N, 2.2%. $^1$H NMR (CD$_3$NO$_2$): δ 8.58 (d (J = 4.4 Hz), 2H, o-HCsH$_3$N), 7.24-7.90 (m, 46H, Cdhrs, HCsH$_3$N), 6.13 (m, 2H, CsH$_4$NCH), 3.62 (m, 8H, THF), 1.79 (m, 8H, THF). $^{31}\text{P}[^1\text{H}]$ NMR (CD$_3$NO$_2$): δ 13.4 (s).

$\text{[Ni(}\mu$-$\eta^3$-$\eta^1$-$\{(\text{C}_6\text{H}_5)p\}_2\text{CHC}_6\text{H}_4\text{N}\}$(C$_4$H$_8$O)$_2$)$_2$·NiCl$_2$·0.85CH$_2$Cl$_2$ (3)

In an attempt to grow crystals of 2, a sample was dissolved in dichloromethane and layered with n-propanol. Over the course of several days, bright green crystals formed which, unfortunately, proved unsuitable for x-ray crystallography. On allowing the supernatant to stand for an additional week, a small quantity of olive-green crystals formed which were shown to be 3 by x-ray crystallography. There was insufficient material available for elemental analysis.

Crystals of 1 and 3, obtained as described above, were mounted on thin glass fibers with a coat of epoxy cement. General procedures for crystal orientation, unit cell determination and refinement and collection of intensity data have been published. Details specific to the present study appear in Table 1. Raw intensity data were corrected for Lorentz and polarization effects, for decay in the intensity monitors (1) and for absorption (3). For 1, the monoclinic cell indicated by the CAD-4 software was confirmed by the observation of 2/m diffraction symmetry and the space group was uniquely determined by the systematic absences observed in the final data set. For 3, no cell of higher than triclinic symmetry was detected and with a reasonable density calculated with Z = 2, P1 was chosen as the space group. This was confirmed by the successful refinement. The position of the copper atom in 1 was obtained from an origin-removed Patterson map and the remainder of the structure developed by successive cycles of refinement followed by calculation of a Δρ map. For 3, the metal atom positions were obtained by direct methods (MULTAN80) and the remainder of the structure developed as for 1. In the latter stages of refinement for 3, a molecule of solvent dichloromethane was found which had an effective occupancy of 0.85 based on refinement of occupancy factors H-atoms were added as fixed contributions in 3 (C-$\text{-H} = 0.98$ Å) with isotropic displacement parameters 1.2 times those of the attached carbon atoms and updated periodically. All computations on 3 employed the MolEN suite of programs running on a VAXstation 3100 computer. The same package was used on 1 until it became evident that the tetrafluoroborate ion was disordered at which point the refinement was completed with SHELXL-93 running on an Insight