tionally (cf. ref 6). At the same time, the base/Co ratio leading to maximum $HCo(CO)_4$ concentration decreases with increasing basicity of the additives $P(OBu)_3$ < py < PBu_3 (Figure 1).

The nitrogen and phosphorus bases catalyzing the hydrogenation of $Co_2(CO)_8$ in our study disproportionate $Co_2(CO)_8$—if applied in stoichiometric amounts—to $[CoB_6][Co(CO)_4]_2$ and $[Co(CO)_nB_{5-n}][Co(CO)_4]$ where B is a N or P base and n = 1, 2, or 3.[7] Halide ions were described to accelerate the disproportionation of cobalt carbonyls.[12] The mechanism of these reactions seems to be rather complex as suggested by some recent results.[13] More information about this disproportionation and about the hydrogenation of $Co_2(CO)_8$ itself is necessary to explain the mechanism of the catalytic effect reported in this work. Kinetic investigations, which are in progress, could contribute to clear some of the open questions.

Acknowledgment. We are grateful to L. Nĕmeth for technical assistance.

Registry No. $Co_2(CO)_8$, 10210-68-1; pyridine, 110-86-1.

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Characterization of an Unusual Binuclear Rhodium Complex with Bridging 2-[Bis(diphenylphosphino)methyl]pyridine (PNP) Ligands

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Summary: An unusual bis(phosphine)-bridged binuclear complex in which the P atoms are arranged trans on one Rh and cis on the other has been synthesized by reaction of $[Rh(Cl)_2(CO)_2]^-$ with PNP ligand in ethanol in the presence of $NaBPh_4$. The single-crystal X-ray structure of $[Rh_2(CO)(\mu\text{-PNP})_2](BPh_4)_2$ has been determined.

Recently there has been considerable interest in the use of bridging bi- and polydentate phosphine and phosphine–pyridine ligands to hold two or more metals in close proximity.[1-6] We have recently reported that 2-[bis(diphenylphosphino)methyl]pyridine, $[Ph_2P]_2CHC_5H_5N$ = PNP, can function as a tridentate ligand to one metal, $[Rh(norbornadiene)(PNP)]PF_6$,[6] or as a bridging bis(phosphine) ligand which gives a binuclear complex of the face-to-face type with trans phosphorus atoms and with the pyridyl nitrogen atoms bound, $[Rh_2(CO)_2(\mu\text{-PNP})_2](PF_6)_2$ (**1**).[5] We now report on the synthesis and characterization of an unusual PNP-bridged binuclear complex of rhodium $[Rh_2(CO)(\mu\text{-PNP})_2](BPh_4)_2$ (**2**), in which the phosphorus atoms are arranged trans on one rhodium and cis on the other (vide infra). This trans,cis phosphorus stereochemistry is very rare among bis(phosphine)-bridged binuclear complexes and has been previously observed only in $[Pt_2(CH_3)_3(\mu\text{-dppm})_2](PF_6)$[7] and in the bis(phosphazane)-bridged complex $[Rh_2(CO)Cl_2\{\mu\text{-(PhO)}_2PN(Et)P(OPh)_2\}_2]$.[8] Therefore, complex **2** is the first structurally characterized example of a bis(phosphine)-bridged binuclear rhodium complex of a simple dppm-type ligand which contains this unusual stereochemistry.

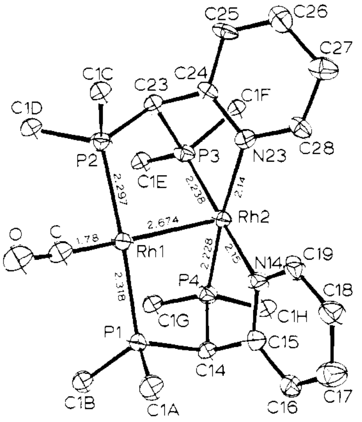
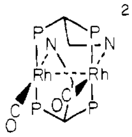
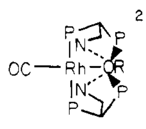


Figure 1. An ORTEP drawing of the dication of $[Rh_2(CO)(\mu\text{-PNP})_2](BPh_4)_2\cdot 2CH_2Cl_2$. Phenyl carbon atoms have been omitted for clarity and are numbered C1A, C2A, ..., C$_6$A for rings A–H. Some selected bond angles and distances are Rh1–Rh2–P3 = 94.9 (1)°, Rh1–Rh2–P4 = 88.7 (1)°, Rh1–Rh2–N14 = 82.3 (3)°, Rh1–Rh2–N23, 97.9 (3)°, Rh2–Rh1–P1 = 92.3 (1)°, Rh2–Rh1–P2, 88.2 (1)°, Rh2–Rh1–C, 166.5 (5)°, P1–Rh1–C = 90.0 (5)°, P2–Rh1–C = 91.2 (5)°, Rh1–C–O, 176 (1)°, and C–O = 1.18 (1) Å.



1



2

The reaction of a stoichiometric amount of PNP ligand[6] dissolved in a minimal amount of CH_2Cl_2 with the lithium salt of $[Rh(CO)_2Cl_2]^{-}$[9] in ethanol saturated with CO resulted in the immediate formation of a red solution. The solution was purged with N_2 and stirred for several hours. A purple precipitate formed upon the addition of an ethanol solution of $NaBPh_4$ and red-orange crystals were obtained by recyrstallization of the precipitate from a CH_2Cl_2–C_2H_5OH solution. The purple color is due to the presence of **1** which is converted into **2** during the recrystallization process. All manipulations were carried out under a purified atmosphere of N_2. The yield of **2** was 70%.[10] ^{31}P NMR of the crude product shows that **2** is

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frequently accompanied by a small amount of **1**.

Since the structure of **2** could not be determined from the spectroscopic data,[10] a single-crystal X-ray analysis was undertaken.[11] The crystal structure consists of well-separated $[Rh_2(CO)(PNP)_2]^{2+}$ dications, BPh_4^- anions, and CH_2Cl_2 solvate molecules. The molecular structure of the dication is shown in Figure 1 along with selected distances and angles. The two rhodium atoms are bonded together with a short separation of 2.674 (1) Å and have different coordination geometries. The one is ca. square planar with trans phosphorus atoms (P1–Rh1–P2 = 172.5 (2)°) and with the CO group positioned ca. trans to the other Rh atom (C–Rh1–Rh2 = 166.5 (5)°). The other Rh atom has an approximate square-pyramidal geometry with cis phosphorus and cis pyridyl nitrogen atoms in the basal plane (P3–Rh2–P4 = 102.1 (2)° and N14–Rh2–N23 = 98.6 (4)°) and with Rh1 occupying the apical position. The phosphorus atoms are trans to the nitrogen atoms in the basal plane (P3–Rh2–N14 = 174.6 (3)° and P4–Rh2–N23 = 173.4 (3)°). The two PNP ligands bridge the Rh atoms, but the four P atoms are not coplanar as is commonly found in this type of complex (e.g., complex **1**). The torsion angles P2–Rh1–Rh2–P3 and P1–Rh1–Rh2–P4 are −36 and 35°, respectively. The square planes around Rh1 and Rh2 are approximately orthogonal with a dihedral angle of 89°. Both pyridyl groups form five-membered PN chelates with the same Rh atom with P–Rh–N bite angles of 77.1 (3) and 82.5 (3)°. The trans Rh–P distances (average 2.308 (4) Å) are similar to values found in dppm- and PNP-bridged binuclear complexes of Rh(I)[5] and the Rh–P distances (Average 2.233 (4) Å) which are trans to nitrogen atoms are shorter due to the decreased trans influence of nitrogen compared with phosphorus. The Rh–N bond distances in **2** (average 2.15 (1) Å) are similar to values found in **1** (2.19 Å)[5] and in $[Rh(nbd)(PNP)]PF_6$ (2.15 Å).[6]

The formation of the Rh–Rh bond in **2** gives a 16-electron count for Rh1 and an 18-electron count for Rh2 assuming that both rhodium atoms are in the +1 oxidation state. The bond distances which involve the rhodium atoms support this assignment. Complex **2** can be converted into **1** by the addition of CO to an acetone solution of **2** at room temperature. Work in progress involves the addition of other small molecules to complex **2** and an investigation of its catalytic properties.

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Registry No. 1, 86307-73-5; 2, 86307-76-8; $[Rh(CO)_2Cl_2]Li$, 86307-77-9; Rh, 7440-16-6.

Supplementary Material Available: Tables of atomic fractional coordinates and thermal parameters for $[Rh_2(CO)(\mu\text{-}PNP)_2]^{2+}$ (55 pages). Ordering information is given on any current masthead page.

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(10) Anal. Calcd for $C_{109}H_{90}N_2OP_4B_2Rh_2$ (**2**): C, 72.93; H, 5.05; N, 1.56; P., 6.90. Found: C, 72.25; H, 5.13; N, 1.57; P. 6.79. **2**: IR (KBr disk) ν(CO) 1982, ν(pyridyl C–N) 1599 cm^{-1}; $^{31}P\{^1H\}$ NMR (acetone solution, 121.5 MHz, ambient temperature) consists of two well-separated doublets of triplets of equal intensity, δ_1 61.5 and δ_2 37.7 vs. external H_3PO_4 with J_d = 136 and 130 Hz, respectively, and J_t = 30.5 and 30.5 Hz.

(11) A red-orange crystal of $2{\cdot}2CH_2Cl_2$ was mounted inside of a sealed capillary tube in its mother liquor (CH_2Cl_2–C_2H_5OH). This procedure was necessary since crystals removed from solution readily lost solvent rendering them unsuitable for X-ray analysis: space group $P\bar{1}$ (No. 2), 23 °C, a =17.011 (8) Å, b = 17.426 (5) Å, c = 18.497 (6) Å, α = 103.34 (3)°, β = 103.23 (4)°, γ = 91.89 (4)°, Z = 2, Mo K$\bar{\alpha}$ graphite monochromatized (λ = 0.71069 Å), CAD 4 diffractometer, ω–2θ scans, $2\theta_{max}$ = 44°, full-matrix least squares, R = 0.085; 6342 reflections with $F_o^2 > 1.0\ \sigma(F_o^2)$, 749 parameters. See ref 5 for details of structure solving package.

Synthesis and Structural Analysis of *trans*-Bis[2-{1,1-bis(methoxycarbonyl)propyl}-pyridine]palladium(II): A Novel, Stable Six-Membered Organopalladium(II) Complex Possessing sp³-Carbon–Metal Bonds

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Summary: The first example of a stable palladium(II) complex having trans, bis[carbon(sp^3)–metal] bonds in a six-membered chelate ring is reported. Synthesis, ^{1}H and ^{13}C NMR spectroscopy, and a single-crystal X-ray structure establish the assignment. It crystallizes in the monoclinic space group $P2_1/n$ with cell constants of a = 10.022 (2) Å, b = 23.820 (4) Å, c = 10.808 (2)Å, β = 107.20 (2)°, and Z = 4. Bond lengths average 2.038 (7) Å for Pd–N and 2.181 (9) Å for Pd–C bonds.

Throughout the past decade, much interest and synthetic effort has been devoted to understand and utilize stable cyclometalated complexes containing transition-metal ions.[2] The five-membered cyclic core **1** has been a common denominator in the majority of such cyclometalated complexes, thus instilling support to the "five-membered ring theory" advanced by Matsuda et al.[3] The rationale for enhanced stability imparted by a five-membered ring is based on the necessity for such complexes to possess a ligand–metal–carbon bond angle (θ) of ca. 90°. While this simple premise appears to have general validity, it by no means precludes other stable multimembered cyclometalated rings. We, as well as others, have demonstrated that at least with one transition metal, palladium, considerable distortions from idealized coordination geometry can occur without undue losses in complex stability or metal–ligand bond character.[4]

To date, few cyclometalated complexes containing a six-membered ring with an N donor have been reported,[5] of these only three possess both pyridine and sp^2 (aromatic) C donor atoms[6] and five possess a N donor and an sp^3-C donor atom.[7] The latter were unstable in solution, and until now no crystal structures or other compelling spectroscopic evidence of formulation have been presented. We herein report the synthesis, spectral correlations, and

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