Inorg. Chem. **2003**, *42*, 3160–3167

Inorganic Chemistry Article

A New Ligand System Based on a Bipyridine-Functionalized Calix[4]arene Backbone Leading to Mono- and Bimetallic Complexes

Reto Dorta,[†] Linda J. W. Shimon,[‡] Haim Rozenberg,[‡] Yehoshoa Ben-David,[†] and David Milstein*,[†]

Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot 76100, Israel, and Unit of Chemical Research Support, The Weizmann Institute of Science, Rehovot 76100, Israel

Received October 28, 2002

The synthesis of a new ligand system for mono- and bimetallic complexes based on a calixarene is described. Ligand BBPC (**3**, bis(bipyridine)-calix[4]arene) is obtained in three steps in 40% overall yield by first brominating one of the methyl groups of the 4,4′-dimethyl-2,2′-bipyridine in two steps and subsequently reacting it with *p-tert*-butylcalix[4]arene under basic conditions. Reaction of BBPC (**3**) with 2 equiv of $[Rh(NBD)_2]BF_4$ or $[Rh(NBD)(CH_3CN)_2]BF_4$ (NBD = norbornadiene) produces the bimetallic compound $BBPC[Rh(NBD)BF_4]_2$ (**4**). Treatment of the ligand with $PdCl_2(CH_3CN)_2$ leads to the isolation of the bimetallic complex $BBPC[PdCl_2]_2$ (**5**). When the nickel precursor $NiBr_2(DME)$ (DME = dimethoxyethane) is reacted with BBPC, the bimetallic complex $BBPC[NiBr_2]_2$ (**6**) is isolated which, upon crystallization from methanol, gives the mononuclear bis(bipyridine) complex BBPC[NiBr(OMe)] (**7**). Full characterization includes X-ray structural studies of complexes **4**, **5**, and **7**. The bimetallic compounds **4** and **5** show metal to metal distances of 4.334 Å (for **4**) and 3.224 Å (for **5**). For all three complexes, unique molecular packing arrangements were found, based on hydrophobic/hydrophilic interactions.

Introduction

The construction of multicomponent molecular systems represents an important first step in the development of new supramolecular systems for catalysis, light-to-energy conversion, and molecular-based devices. In catalysis, cooperative reactivity between multiple metal centers is commonly postulated for enzymatic systems as well as for heterogeneous catalysts and has evolved into an intriguing design principle for synthetic catalysts.[1] Thus, the area of bi- or polymetallic cooperativity in homogeneous catalysis is growing rapidly, and the proximity of metal centers was shown to favor advantageous alternatives for substrate activation and subsequent reactions in homobimetallic systems[2] and in the catalysis by monolayers.[3] We decided to synthesize a ligand system for this purpose using the bipyridine unit as a chelating ligand and the calix[4]arene as a relatively rigid backbone.[4] Although bipyridine derivatives have been introduced on both lower and upper rims of calixarenes,[5] relatively few complexation studies with transition metals were described and characterization of such complexes by X-ray crystallography is rare.[6] To the best of our knowledge, the complexation behavior of bipyridine−calixarene systems toward rhodium and palladium has never been reported despite the importance of these compounds as catalyst precursors for various transformations.[7]

In this paper we report the synthesis of a new ligand system, the 1,3-alternate, lower rim compound BBPC (bis(bipyridine)-*p-tert*-butylcalix[4]arene) bearing two opposite 4,4′-dimethyl-2,2′-bipyridine ligand units on the *p-tert*-

---

* Author to whom correspondence should be addressed. E-mail: david.milstein@weizmann.ac.il.

[†] Department of Organic Chemistry.

[‡] Unit of Chemical Research Support.

[1] (a) *Catalysis by Di- and Polynuclear Metal Cluster Complexes*; Adams, R. A., Cottton, F. A., Eds.; Wiley-VCH: New York, 1998. (b) Braunstein, P.; Rosé, J. In *Metal Clusters in Chemistry*; Braunstein, P., Oro, L. A., Raithby, P. R., Eds.; Wiley-VCH: Weinheim, Germany, 1999; p 616.

[2] For representative examples: (a) Broussard, M. E.; Juma, B.; Train, S. G.; Peng, W.-J.; Laneman, S. A.; Stanley, G. G. *Science* **1993**, *260*, 1784−1788. (b) Konsler, R. G.; Karl, J.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1998**, *120*, 10780−10781. (c) Cai, L.; Mahmoud, H.; Han, Y. *Tetrahedron: Asymmetry* **1999**, *10*, 411−427. (d) He, C.; Lippard, S. J. *J. Am. Chem. Soc.* **2000**, *122*, 184−185.

[3] Toellner, K.; Popovitz-Biro, R.; Lahav, M.; Milstein, D. *Science* **1997**, *278*, 2100−2103.

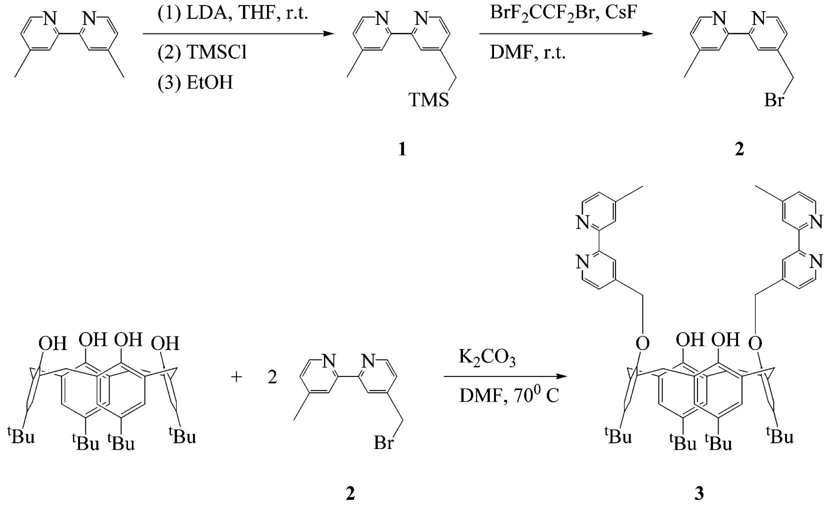
[4] For a review on the use of bipyridine as a ligand in metal complexation, see: Kaes, C.; Katz, A.; Hosseini, M. W. *Chem. Rev.* **2000**, *100*, 3553−3590.

[5] For a review on calixarenes, see: Wieser, C.; Dieleman, C. B.; Matt, D. *Coord. Chem. Rev.* **1997**, *165*, 93−161.

[6] For a monometallic copper(I) complex, see: (a) Regnouf-de-Vains, J.-B.; Lamartine, R.; Fenet, B.; Bavoux, C.; Thozet, A.; Perrin, M. *Helv. Chim. Acta* **1995**, *78*, 1607−1619. For a monometallic cobalt(II) complex, see: (b) Dalbadie, J.-O.; Regnouf-de-Vains, J.-B.; Lamartine, R.; Lecocq, S.; Perrin, M. *Eur. J. Inorg. Chem.* **2000**, 683−691. For a monometallic rhenium complex, see: (c) Cooper, J. B.; Drew, M. G. B.; Beer, P. D. *J. Chem. Soc., Dalton Trans.* **2001**, 392−401. For bimetallic complexes, see: (d) Dalbadie, J.-O.; Regnouf-de-Vains, J.-B.; Lamartine, R.; Perrin, M.; Lecocq, S.; Fenet, B. *Eur. J. Inorg. Chem.* **2002**, 901−909.

10.1021/ic020643a CCC: $25.00

Scheme 1. Synthetic Pathway to Ligand BBPC (**3**)



butylcalix[4]arene backbone. We report our findings regarding the reactivity of BBPC (**3**) toward Rh(I), Pd(II), and Ni(II) metal precursors which gave rise to the expected homobimetallic complexes. In the case of the harder, first-row Ni(II) compound, a monometallic bis(bipyridinyl)nickel(II) was obtained upon crystallization in methanol. Full characterization of the resulting compounds includes the single-crystal X-ray structures of three of the complexes revealing unusual molecular packing arrangements. In the case of the bimetallic systems, metal-to-metal distances of 4.334 Å (for rhodium) and 3.224 Å (for palladium) were found.

Results and Discussion

The synthesis of the new ligand system was accomplished in three steps using the commercially available 4,4′-dimethyl-2,2′-bipyridine (Scheme 1). The preparation of the mono(bromomethyl) derivative is typically done by radical halogenation.[8] Unfortunately, this method gives rise to mixtures of halogenated products that are very difficult to separate by column chromatography. We therefore decided to synthesize the compound using a two-step procedure adapting a synthetic scheme published recently for the double halogenation of dimethylbipyridines.[9] As pointed out by the authors, monolithiation is often complicated by over- or underfunctionalization of dimethylbipyridine leading to mixtures of products. Despite this, we have found conditions where compound **1** could be obtained in reasonable yield (Scheme 1).

Thus, deprotonation of 4,4′-dimethyl-2,2′-bipyridine by a slight excess of LDA (LDA = lithium diisopropylamide) was carried out at room temperature and was followed by quenching with (TMS)Cl ((TMS)Cl = trimethylsilyl chloride). Subsequent workup and chromatography gave **1** in 60% yield as a white solid. The second step consisted of the removal of the TMS group with CsF in dry DMF giving rise to a highly basic, carbanion-like functionality which was subsequently brominated in situ by the electrophile BrF_2-CCF_2Br. Compound **2** was thus obtained as a pure compound in high yield without the need for chromatographic workup. Although the overall yield for these two steps did not exceed the one reported for the direct, radical bromination with NBS, we found this synthetic procedure much more practical and overall less time-consuming. In the third step, as shown in Scheme 1, the *p-tert*-butylcalix[4]arene backbone was reacted with 4-(bromomethyl)-4′-methyl-2,2′-bipyridine (**2**) under basic conditions leading to the formation of the desired ligand BBPC (**3**) in almost quantitative yield. Characterization of **3** by mass spectrometry clearly showed the molecular peak at *m*/*z* 1014 [M^+]. The cone conformation of the ligand was confirmed by the large chemical shift difference of the anchors' methylene bridges in the ^1H NMR spectrum. In addition, a $^1H-^{15}N$ GHMBC measurement was carried out showing two signals for the four nitrogen atoms of BBPC (**3**) at 240.2 and 245.4 ppm.[10]

Complexation of Rhodium. We chose cationic rhodium precursors for complexation with the ligand BBPC (**3**) in view of the importance of [(bipy)Rh]$^+$ compounds in catalytic hydrogenation and hydrogen transfer reactions. Furthermore, we have recently shown that thin films of these complexes indeed gave increased catalytic activities and

---

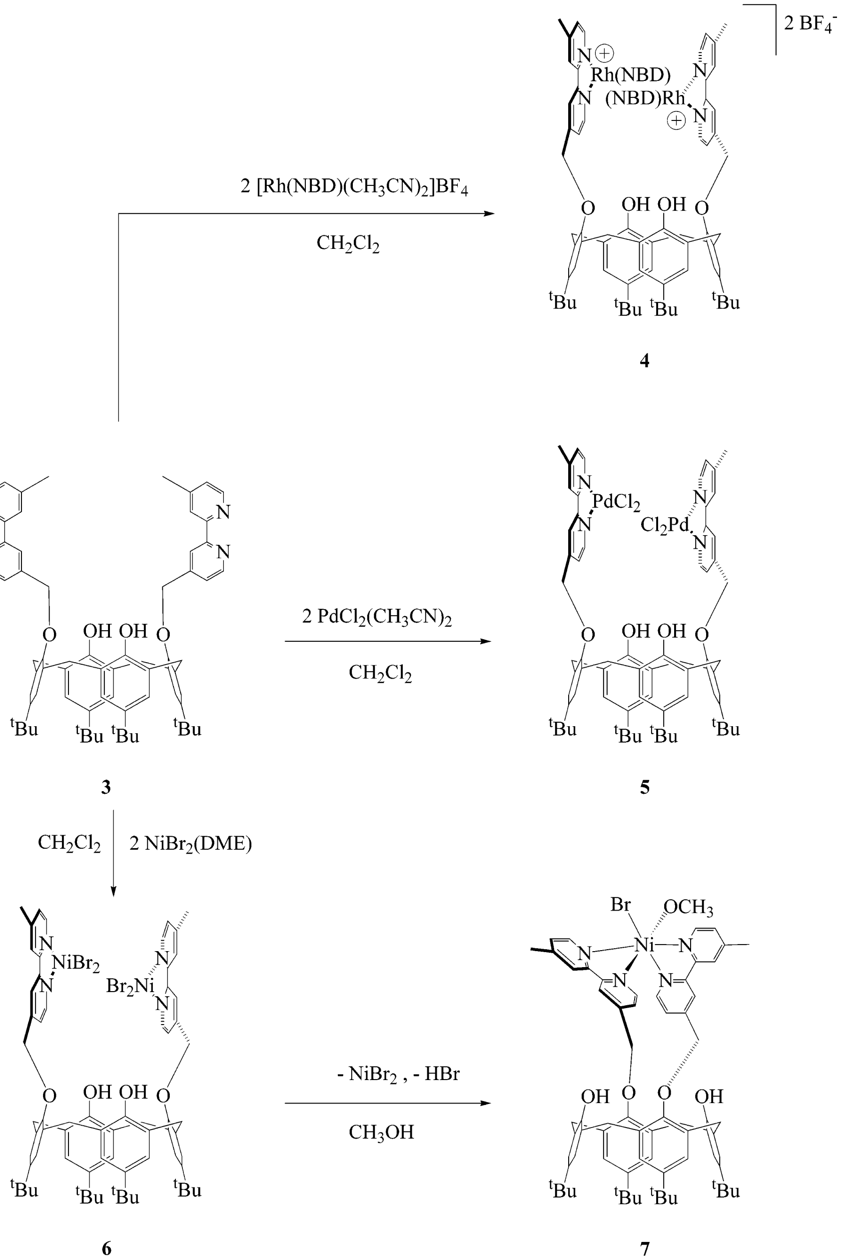
(7) For the use of cationic rhodium systems in hydrogenation and hydrogen transfer reactions of olefins and ketones, see: (a) Zassinovich, G.; Mestroni, G.; Gladiali, S. *Chem. Rev.* **1992**, *92*, 1051−1069. (b) Mestroni, G.; Spogliarich, R.; Camus, A.; Martinelli, F.; Zassinovich, G. *J. Organomet. Chem.* **1978**, *157*, 345−352. (c) Mestroni, G.; Zassinovich, G.; Camus, A. *J. Organomet. Chem.* **1977**, *140*, 63−72. For the copolymerization of CO/olefins using bipyridine−palladium systems, see: (d) Brookhart, M.; Wagner, M. I.; Balavoine, G. G. A.; Haddou, H. A. *J. Am. Chem. Soc.* **1994**, *116*, 3641−3642. (e) Drent, E.; Budzelaar, P. H. M. *Chem. Rev.* **1996**, *96*, 663−681 and references therein. (f) Milani, B.; Anzilutti, A.; Vicentini, L.; Sessanta o Santi, A.; Zangrando, E.; Geremia, S.; Mestroni, G. *Organometallics* **1997**, *16*, 5064−5075. For reviews on Pd(II)− and Ni(II)−diimine systems for the polymerization of olefins, see: (g) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169−1203 and references therein. (h) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428−447 and references therein.

(8) Gould, S.; Strouse, G. F.; Meyer, T. J.; Sullivan, B. P. *Inorg. Chem.* **1991**, *30*, 2942−2949.

(9) (a) Fraser, C. L.; Anastasi, N. R.; Lamba, J. J. S. *J. Org. Chem.* **1997**, *62*, 9314−9317. (b) Savage, S. A.; Smith, A. P.; Fraser, C. L. *J. Org. Chem.* **1998**, *63*, 10048−10051.

(10) For a recent review on the use of $^1H-^{15}N$ GHMBC measurements for the structural elucidation of compounds, see: Martin, G, E.; Hadden, C. E. *J. Nat. Prod.* **2000**, *63*, 543−585.

Scheme 2. Complexation Behavior of Ligand BBPC (**3**) toward Rh, Pd, and Ni Precursors



surprising selectivity,[3] thus showing the impact of cooperative effects in catalysis for such complexes. Upon addition of 0.5 equiv of BBPC (**3**) to a stirred dichloromethane solution of $[Rh(NBD)_2]BF_4$ or $[Rh(NBD)(CH_3CN)_2]BF_4$ (NBD = norbornadiene), a color change from red to pink was observed and precipitation by slow addition of diethyl ether resulted in the isolation of BBPC$[Rh(NBD)BF_4]_2$ (**4**) in nearly quantitative yield (Scheme 2). Complex **4** was characterized by elemental analysis and by using various NMR techniques. The ^{1}H NMR spectrum of **4** showed six resonances in the aromatic region attributable to the nonequivalent parts of the ligand unit, one resonance for the equivalent aromatic proton signals of the calix[4]arene backbone, and a singlet arising from the phenolic protons. The bridging methylene groups of the calix[4]arene gave rise to an AB system with two separate doublet signals at $\delta = 4.37$ ppm and $\delta = 3.62$ ppm ($J = 13.1$ Hz), respectively. Various ^{13}C NMR techniques allowed the assignment of all the carbon signals and full characterization included a ^{1}H$-^{15}$N GHMBC measurement. The resulting spectrum clearly showed the two signals of the nitrogen atoms of the ligand in BBPC$[Rh(NBD)BF_4]_2$ (**4**). The correlation provided their ^2J and ^3J couplings to the neighboring hydrogen atoms. Very clear shifts of 40$-$50 ppm in the ^{15}N spectrum were seen compared to the free ligand. Furthermore, coordination of the nitrogen atoms to the rhodium metal gave rise to coupling constants of $J_{N-Rh} = 19.8$ and 20.0 Hz, respectively.[11] Interestingly, when the reaction of ligand **3** with only 1 equiv of $[Rh(NBD)_2]BF_4$ or $[Rh(NBD)(CH_3CN)_2]BF_4$ in CD_2Cl_2 in an NMR tube was monitored, the bipyridine moiety showed broad peaks in the aromatic region, suggesting some

---

[11] Characterization of rhodium complexes using this method was recently reported; see: Dorta, R.; Konstantinovski, L.; Shimon, L. J. W.; Ben-David, Y.; Milstein, D. *Eur. J. Inorg. Chem.* **2003**, 70.

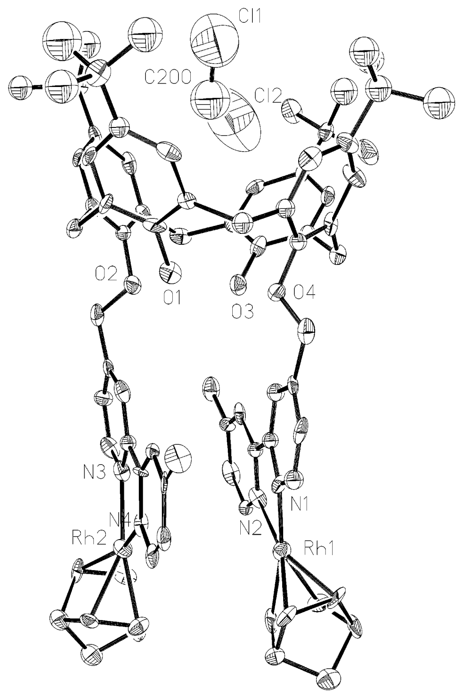


Figure 1. ORTEP drawing of a molecule of **4** (50% of probability). BF_4^-, solvent molecules (except entrapped CH_2Cl_2), and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Rh(1)−N(1) 2.079(11), Rh(1)−N(2) 2.053(12), Rh(1)−C(11) 2.111(14), Rh(1)−C(12) 2.114(14), Rh(1)−C(13) 2.121(13), Rh(1)−C(14) 2.121(14), Rh(2)−N41) 2.081(12), Rh(2)−N(3) 2.080(12), Rh(2)−C(21) 2.107(14), Rh(2)−C(23) 2.110(14), Rh(2)−C(24) 2.117(13), Rh(2)−C(22) 2.126(14); N(2)−Rh(1)−N(1) 78.0(5), N(1)−Rh(1)−C(11) 153.2(6), N(2)−Rh(1)−C(12) 105.4(6), C(11)−Rh(1)−C(12) 38.1(5), N(1)−Rh(1)−C(13) 101.9(5), N(2)−Rh(1)−C(14) 164.1(6), C(13)−Rh(1)−C(14) 38.1(5), N(4)−Rh(2)−N(3) 77.3(7), N(3)−Rh(2)−C(21) 105.8(6), N(4)−Rh(2)−C(23) 106.6(7), C(21)−Rh(2)−C(23) 67.4(6), N(3)−Rh(2)−C(24) 154.4(6), N(4)−Rh(2)−C(22) 157.5(5), C(23)−Rh(2)−C(22) 79.0(6), C(24)−Rh(2)−C(22) 66.6(6).

kind of dynamic process at room temperature in such a monometallic species. Addition of another 1 equiv of metal precursor immediately gave rise to sharp peaks corresponding to the bimetallic complex **4**. To unambiguously ascertain the exact structure of complex **4**, crystals suitable for an X-ray crystallographic analysis were grown by slow diffusion of diethyl ether into a concentrated solution of **4** in a dichloromethane/acetonitrile mixture (10/1). Complex **4** crystallizes in the orthorhombic spacegroup *Pbca* with two molecules of dichloromethane and one molecule of acetonitrile. The ORTEP drawing is shown in Figure 1 alongside with a list of selected bond lengths and angles. As expected, both rhodium atoms in complex **4** are located in the center of a square planar arrangement with two double bonds of the NBD ligand trans to the corresponding pyridine moieties of the bipyridine units. The two pendant pyridyl arms are parallel to each other, and their distances suggest some π-stacking between them. Spatially, the two bipyridine moieties point at opposite directions. An interesting fact is that despite the bulky NBD ligands on the two metals, the distance between the two rhodium atoms is relatively small at 4.334 Å. Another remarkable feature is the entrapment of one dichloromethane solvent molecule inside the cavity of the calix[4]arene part with the CH_2 group pointing inward and the two chlorine atoms pointing toward the outside of the hydrophobic calixarene pocket. The crystal packing of molecules of complex **4** is shown in Figure 2. Interestingly, we observe the formation of bilayers of molecules of **4** with, on both ends, the hydrophobic calixarene part and in the center the hydrophilic metal-containing bipyridine part. These layers face each other and form chains of alternating, intercalated molecules of **4**. The planar $Rh(bipy)^+$ moieties in these chains are almost perfectly parallel to each other, and the perfect packing of the chains is seen in the hydrogen-bonding interaction between the methylbipyridine moiety of one of the molecules and the adjacent rhodium atom, with a distance of Rh···H = 2.727 Å (not shown in Figure 2). The angle between the Rh(bipy) planes of the two chains is 53.7°. Both BF_4^- counterions are sandwiched between two adjacent complexes (not shown).

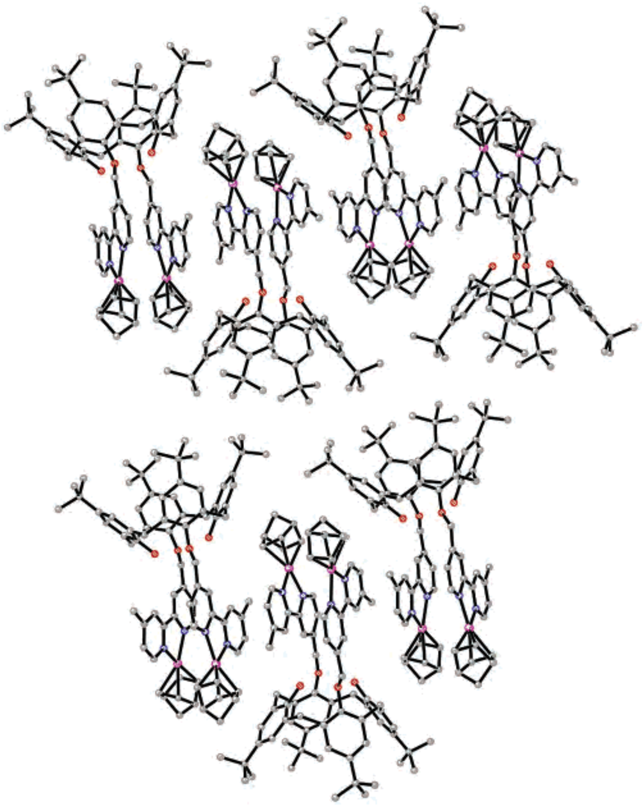


Figure 2. View of the crystal packing in complex **4**.

Complexation of Palladium. The next metal we checked for complexation to ligand BBPC (**3**) was palladium. When 2 equiv of $PdCl_2(CH_3CN)_2$ in dichloromethane was added to **3** (in dichloromethane), an immediate color change from deep yellow to pale beige occurred (Scheme 2). The solution was left stirring at room temperature for 3 h during which time partial formation of an off-white precipitate was observed. After workup, the bimetallic complex BBPC-$[PdCl_2]_2$ (**5**) could be isolated as an off-white solid in high yield. Although the solubility of complex **5** in common organic solvents is low, the ^1H NMR spectrum in pyridine-d_5 supported the formulation with one set of peaks for the metal-coordinated bipyridine moiety showing significant shifts compared to the spectrum of the free ligand recorded in the same solvent. Furthermore, coordination of the palladium to the bipyridine moiety gave rise to shifts of the

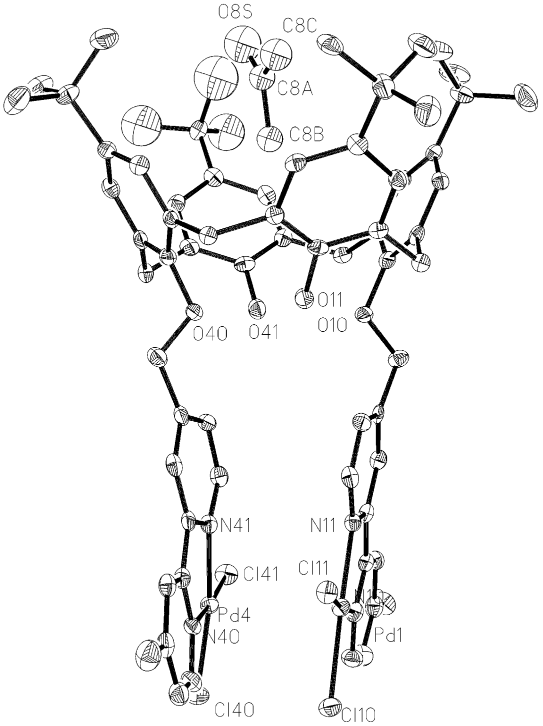


Figure 3. ORTEP drawing of a molecule of **5** (50% of probability, one of two independent molecules). Solvent molecules (except entrapped acetone) and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Pd(1)−N(10) 2.025(4), Pd(1)−N(11) 2.026(4), Pd(1)−Cl(11) 2.2822(15), Pd(1)−Cl(10) 2.2893(16), Pd(1)···Pd(4) 3.2579(8), Pd(4)−N41) 2.030(4), Pd(4)−N(40) 2.020(4), Pd(4)−Cl(40) 2.2928(16), Pd(4)−Cl(41) 2.2889(16); N(10)−Pd(1)−N(11) 80.60(18), N(10)−Pd(1)−Cl(11) 174.53(13), N(11)−Pd(1)−Cl(11) 94.00(13), N(10)−Pd(1)−Cl(10) 94.98(14), N(11)−Pd(1)−Cl(10) 175.46(13), Cl(11)−Pd(1)−Cl(10) 90.40(5), N(40)−Pd(4)−N(41) 80.73(18), N(40)−Pd(4)−Cl(41) 174.87(13), N(41)−Pd(4)−Cl(41) 94.17(13), N(40)−Pd(4)−Cl(40) 94.72(13), N(41)−Pd(4)−Cl(40) 171.73(13), Cl(41)−Pd(4)−Cl(40) 90.27(5).

py-CH_2-O (5.14 ppm) and the py-CH_3 (2.13 ppm) groups of the ligand compared to free BBPC (**3**) and to complex **4**. The formulation of **5** was also supported by elemental analysis and complete characterization included an X-ray crystallographic analysis. Yellow crystals suitable for X-ray diffraction were obtained by direct reaction of the metal precursor with the ligand in an acetone solution at room temperature. An ORTEP drawing of one of the two independent molecules of **5**, together with selected bond lengths and angles, is given in Figure 3. The complex crystallizes in the triclinic space group $P\bar{1}$ with two molecules of **5**/asymmetric unit. Furthermore, we find 10 molecules of solvent (acetone)/unit. As shown in Figure 3, one of these acetone molecules is trapped inside the calixarene cavity, with one of the CH_3 groups pointing into the hydrophobic pocket and the oxygen atom, as expected, pointing outward. Each palladium atom is located in a nearly perfectly square planar environment binding to one of the bipyridine units and to two chloride atoms. Mean bond lengths of Pd−N 2.03 Å and Pd−Cl 2.29 Å compare well with the ones found for the parent compound $PdCl_2$(bpy) (bpy = 2,2′-bipyridine).[12] In complex **5**, the two palladium atoms are at an average distance of 3.224 Å. The importance of ligand BBPC (**3**) in bringing the two metals close together thus becomes very apparent when comparing the Pd···Pd of complex **5** with $PdCl_2$(bpy) and $PdBr_2$(bpy).[12,13] Both these complexes show large distances between adjacent metal atoms in the solid state of 4.587(2) and 5.246(1) Å, respectively. The shorter metal-to-metal distance of **5** compared to **4** is without a doubt rendered possible because the chloride atoms trans to the pyridine fragments in these square-planar complexes sterically allow the closer approach of the two metal atoms. The view in Figure 4 shows that the ligand molecules indeed pack in a way as to ensure layers of the hydrophobic part pointing at each other and the hydrophilic part with the metal sandwiched between them. A view along the Pd−Pd axis reveals a perfectly parallel arrangement of the bipyridine rings to each other, although they point to opposite directions. Again, the orientation of the rings toward the opposite sides permits a reduced distance of the two metal atoms.

Complexation of Nickel. We decided to check the complexation behavior of our ligand **3** toward the first-row metal nickel. To synthesize the nickel complex, we followed a procedure recently reported for the parent bipyridine complex,[14] which involves reaction of the metal precursor $NiBr_2$(DME) (DME = $MeOCH_2CH_2OMe$) with BBPC (**3**) in dichloromethane. After the mixture was stirred at room temperature for 2 days, a greenish solid was obtained which was washed with diethyl ether and dried. The composition of this complex as being the expected bimetallic compound BBPC$[NiBr_2]_2$ (**6**) was confirmed by elemental analysis (Scheme 2). When compound **6** was dissolved in methanol and left standing overnight, green crystals formed in low yield. The crystals were subjected to an X-ray crystallographic analysis which showed, surprisingly, the monometallic complex BBPC[NiBr(OCH_3)] (**7**). This complex was most probably formed by reaction of **6** with methanol with concomitant loss of 1 equiv of $NiBr_2$ and HBr. In fact, HBr cocrystallizes with **7** in the unit cell and details of the structure can be found in the Supporting Information. The ORTEP view of complex **7** with the atomic numbering scheme, together with selected bond lengths and angles, is shown in Figure 5. As in the case of complexes **4** and **5**, the calixarene platform subunit displays a cone conformation. The molecular structure of complex **7** contains one Ni(II) atom with distorted cis-octahedral coordination formed by the two chelating bipyridine arms of the ligand, one bromide ligand, and one methoxy unit. Although such a 20-electron configuration is common in nickel complexes, only very few bis(bipyridine) complexes of this type have been studied by X-ray crystallography.[15] The Ni−N_{bipy} bond distances (mean value 2.090 Å) agree well with those reported previously for other nickel(II) complexes containing bipy. As expected,

---

(12) Canty, A, J.; Skelton, B. W.; Traill, P. R.; White, A. H. *Aust. J. Chem.* **1992**, *45*, 417.

(13) Smeets, W. J. J.; Spek, A. L.; Hoare, J. L.; Canty, A. J.; Hovestad, N.; van Koten, G. *Acta Crystallogr.* **1997**, *C53*, 1045.

(14) Killian, C. M.; Johnson, L. K.; Brookhart, M. *Organometallics* **1997**, *16*, 2005−2007.

(15) (a) Osakada, K.; Yamamoto, T.; Yamamoto, A.; Takenaka, A.; Sasada, Y. *Acta Crystallogr.* **1984**, *C40*, 85. (b) Urtiaga, M. K.; Pizarro, J. L.; Cortes, R.; Aintzane, G.; Larramendi, J. I. R. *Acta Crystallogr.* **1994**, *C50*, 56. (c) Fernandez-Gonzalez, N.; Gonzalez-Silgo, C.; Gonzalez-Plata, J.; Gili, P.; Martin-Zarza, P. *Acta Crystsllogr.* **2001**, *E57*, m43.

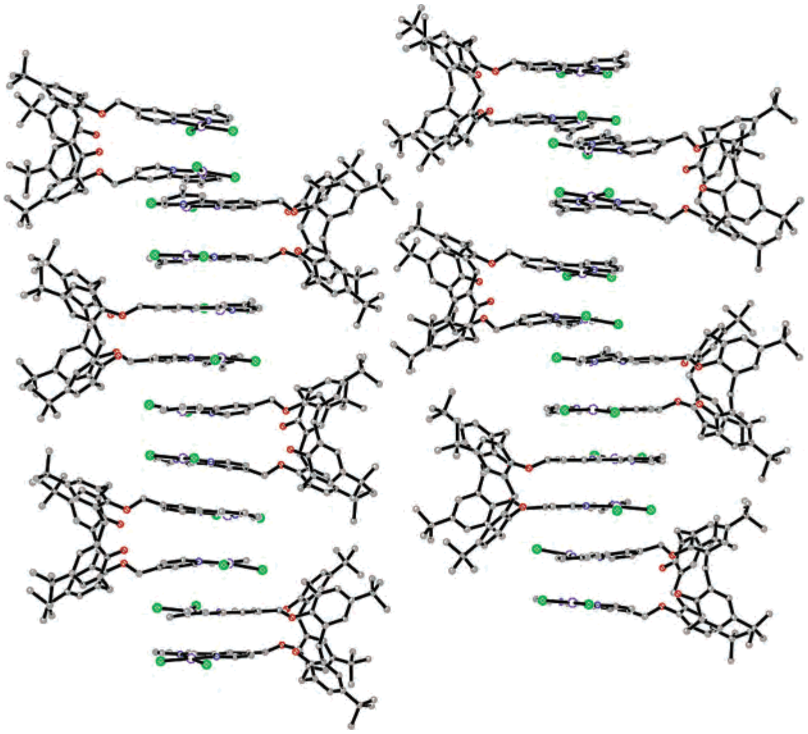


Figure 4. View of the crystal packing in complex **5**.

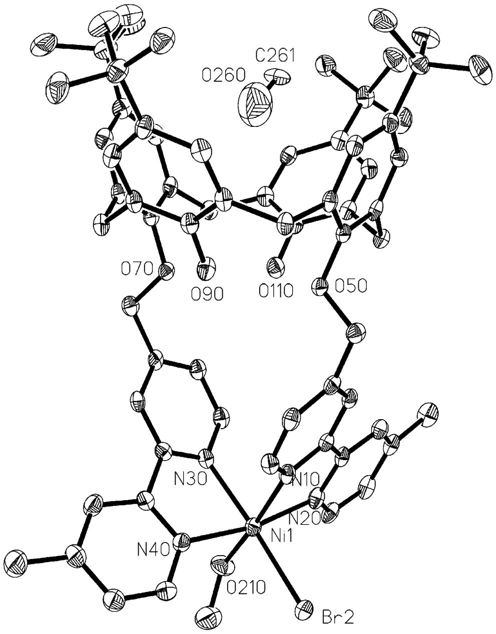


Figure 5. ORTEP drawing of a molecule of **7** (50% of probability). Solvent molecules (except entrapped methanol) and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni(1)−N(20) 2.057(4), Ni(1)−N(40) 2.074(4), Ni(1)−N(10) 2.081(4), Ni(1)−O(210) 2.092(3), Ni(1)−N(30) 2.148(4), Ni(1)−Br(2) 2.5103(7); N(20)−Ni(1)−N(40) 169.31(15), N(20)−Ni(1)−N(10) 79.44(14), N(40)−Ni(1)−N(10) 95.89(14), N(20)−Ni(1)−O(210) 92.86(14), N(10)−Ni(1)−O(210) 169.09(14), N(20)−Ni(1)−N(30) 91.85(14), N(40)−Ni(1)−N(30) 77.98(14), N(10)−Ni(1)−N(30) 83.16(14), O(210)−Ni(1)−N(30) 89.44(14), N(20)−Ni(1)−Br(2) 93.88(10), N(40)−Ni(1)−Br(2) 96.09(10), N(10)−Ni(1)−Br(2) 94.58(10), O(210)−Ni(1)−Br(2) 93.63(10), N(30)−Ni(1)−Br(2) 173.35(10).

both bipy ligands are nearly planar and the mean planes of the two bipyridine moieties are inclined by 71.67° with respect to one another. The bond distance Ni−N(3) is longer than for the other nitrogen atoms (2.148(4) Å) due to influence of the bromide atom trans to it. Again, molecules of **7** crystallize with solvents (in this case, eight molecules of methanol) with one of them entrapped in the calix[4]arene pocket as shown in Figure 5.

Although complex **7** is monometallic, the study of the crystal packing of **7** reveals an arrangement very similar to the ones seen for **4** and **5**, displaying an arrangement which maximizes packing by positioning the hydrophilic, metal-containing parts of the molecules close to each other. This again leads to layers of molecules with alternating disposition of the complexes with respect to the axis defined by the layers. The hydrophobic calixarene part of the ligands of neighboring layers are again in close contact with each other (see Supporting Information).

Summary

We have reported the synthesis of a new ligand system for mono- and bimetallic complexation on the basis of the clean incorporation of two bipyridine units at the lower rim of the *p*-*tert*-butylcalix[4]arene platform. Selective bromination of only one methyl group of the initial 4,4′-dimethyl-2,2′-bipyridine unit was achieved in a two-step procedure which turned out to be more convenient than the previously known methods. Bimetallic late transition metals were thus easily obtained by reacting ligand BBPC (**3**) with cationic Rh(I)−diene or neutral palladium and nickel halide precursors giving complexes **4**−**6**. The monometallic nickel complex **7** was obtained by simple dissolution of **6** in methanol. Complete characterization includes the X-ray crystallographic study of complexes **4**, **5**, and **7**. All of these complexes show unique molecular packing arrangements, arising from hydrophilic/hydrophobic interactions in these systems. Furthermore, the rigidity of the calix[4]arene backbone of ligand BBPC (**3**) allows the close approach of the metal centers as seen in the X-ray structures of complexes **4** and **5**. The binuclear complexes **4**−**6** are thus an ideal starting point for future catalytic studies with these systems, insofar as the parent mononuclear compounds are known catalysts for various transformations. This is the subject of ongoing research in our laboratories.

Experimental Section

General Procedures. All experiments were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres glovebox equipped with a MO 40-2 inert gas purifier. All solvents were reagent grade or better. All nondeuterated solvents were refluxed over sodium/benzophenone ketyl and distilled under argon atmosphere. Deuterated solvents were used as received. All the solvents were degassed with argon and kept in the glovebox over molecular sieves. Commercially available reagents were used as received. The complexes $[Rh(NBD)_2]BF_4$ and $[Rh(NBD)(CH_3CN)_2]$-BF_4 were prepared according to literature procedures.[16]

^1H and ^{13}C (DEPT) 1D NMR spectra were recorded on a Bruker DPX-250 spectrometer. A Bruker DRX-400 spectrometer operating at 400.13 MHz (^1H), 100.61 MHz (^{13}C), or 40.54 MHz (^{15}N) was used for 2D spectra. The spectrometer was equipped with a 5-mm Bruker inverse multinuclear resonance probe with a single-axis (z) gradient coil. Measurements were carried out at a probe temperature of 25 °C using concentrations of ca. 20 mg/mL. 2D $^1H-^{13}C$ correlation spectra were acquired with 1K points in F_2, 128−256 complex increments in F_1, and 4−8 scans/increment for GHMQC and 1−2K points in F_2, 128−256 increments in F_1, and 8−16 scans for GHMBC experiments. 2D $^1H-^{15}N$ correlation spectra were measured using the Bruker standard microprogram GHMBC. The GHMBC spectra were collected with 2K × 256 (512) data points and 96−120 scans for each increment using the spectral widths in F_1 and F_2 of ca. 8−9 ppm for proton and 100−300 ppm for nitrogen-15. The long-range delay was optimized for 50−60 ms. Apodization was done with a sine bell in both dimensions. All ^{15}N spectra were referenced to liquid ammonia. Abbreviations used in the description of NMR data are as follows: b, broad; s, singlet; d, doublet; t, triplet; m, multiplet. Elemental analyses were performed by H. Kolbe, Mikroanalytisches Laboratorium, 45470 Mühlheim, Germany.

Synthesis of 4-(Trimethylsilyl)-4′-methyl-2,2′-bipyridine (1). A solution of *n*-BuLi (1.43 M in hexane, 39.5 mL, 56.48 mmol) was added dropwise via syringe to a solution of diisopropylamine (8 mL) in THF (30 mL) and was stirred at room temperature for 15 min. 2,2′-Dimethyl-4,4′-bipyridine (10.00 g, 54.35 mmol) dissolved in THF (250 mL) was then added via cannulation, and the resulting deep red solution was stirred for 2 h at room temperature before addition of (TMS)Cl (7.53 g, 69.34 mmol). The reaction mixture was quenched after 1 min by adding EtOH (16.4 mL) and was stirred for another 15 min. Saturated aqueous $NaHCO_3$ (500 mL) was added, and the product was extracted with EtOAc (3 × 1000 mL). The combined organic layers were washed with brine until neutral, dried over Na_2SO_4, filtered, and concentrated in vacuo. Chromatography was performed on a deactivated silica column (pretreated with 10% triethylamine in hexane and subsequently washed with hexane). Elution with 3−5% EtOAc/hexane yielded the desired compound as the second fraction, the first one being the di-TMS product and the third being the starting material. The combined organic fractions of the desired compound were dried over Na_2SO_4, filtered, and concentrated in vacuo to give a white crystalline solid. Yield: 8.35 g, 60%. ^1H NMR (CD_2Cl_2): δ = 0.00 (s, 9H), 2.18 (s, 2H), 2.40 (s, 3H), 6.91 (dd, 1H, 5.0 and 1.8 Hz), 7.09 (m, 1H), 8.01 (s, 1H), 8.19 (s, 1H), 8.44 (d, 1H, 5.0 Hz), 8.50 (d, 1H, 5.0 Hz) ppm.

Synthesis of 4-(Bromomethyl)-4′-methyl-2,2′-bipyridine (2). 1,2-Dibromotetrafluoroethane (6.2 mL, 51.90 mmol) followed by CsF (7.4 g, 48.72 mmol) was added to a solution of **1** (6.20 g, 24.18 mmol) in DMF (250 mL). The solution was stirred for 2.5 h and then poured into a mixture of EtOAc/H_2O (1600 mL each) followed by additional extraction of the H_2O layer (3 × 550 mL EtOAc). The combined organic layers were washed twice with H_2O, filtered, and concentrated in vacuo. Recrystallization from a hot pentane solution yielded the desired product as almost colorless crystals. Yield: 5.23 g, 82%. ^1H NMR (CD_2Cl_2): δ = 2.41 (s, 3H), 4.45 (s, 2H), 7.12 (m, 1H), 7.30 (dd, 1H, 5.0 and 1.8 Hz), 8.20 (s, br, 1H), 8.38 (s, 1H), 8.51 (d, 1H, 5.0 Hz), 8.62 (d, 1H, 5.0 Hz) ppm.

Synthesis of BBPC (3). A mixture of *p-tert*-butylcalix[4]arene (0.60 g, 0.93 mmol), **2** (1.29 g, 4.90 mmol), and anhydrous K_2CO_3 (0.60 g, 4.34 mmol) was added to DMF (30 mL) in a Schlenk flask. The solution was heated at 70 °C and left for 20 h stirring under an argon atmosphere. The dark red-brown reaction mixture was then poured over H_2O (200 mL), and the resulting precipitate was filtered. It was the dissolved in $CHCl_3$, washed with H_2O, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude residue was loaded onto a silica gel column (ICN, 60−100 MESH, deactivated with $CHCl_3$/10% Et_3N and washed with $CHCl_3$ before use) and was eluted with $CHCl_3$. Product **3** was dried in vacuo, redissolved in hexane, filtered over filter paper, and concentrated in vacuo. Yield: 0.87 mg, 94%. ^1H NMR (C_6D_6): δ = 1.01 and 1.37 (s each, 18H each, ^{t}Bu-CH_3), 2.48 (s, 6H, Py-CH_3), 3.42 and 4.37 (d each, 4H each, Ar-CH_2, J = 13.1 Hz), 5.23 (s, 4H, ArO-CH_2), 6.88 and 7.16 (s each, 4H each, Ar H), 7.20 (s, 2H, Ar−OH), 8.16 (d, 2H, Py H, 5 Hz), 8.36 (s, 2H, Py H), 8.45 (s, 2H, Py H), 8.56 (d, 2H, 5.0 Hz), 8.72 (d, 2H, Py H, 5,0 Hz) ppm. ^{15}N NMR (CD_3OD): δ = 240.20 (s, 2N, ^2J and ^3J with py H), 245.40 (s, 2N, ^2J and ^3J with py H) ppm. MS (EI): found, m/z 1014 [M^+]; calcd for $C_{68}H_{76}N_4O_4$, m/z 1013.45.

Preparation of BBPC[Rh(NBD)BF$_4$]$_2$ (4). A solution of [Rh-(NBD)(CH_3CN)$_2$]BF_4 (43.0 mg, 0.118 mmol) in CH_2Cl_2 (2 mL) was added to a solution of ligand **3** (60.0 mg, 0.059 mmol) in CH_2Cl_2 (3 mL). The resulting dark red solution was stirred at room temperature for 1 h. Slow addition of diethyl ether led to the precipitation of a red microcrystalline solid which was decanted, washed with additional diethyl ether, and dried in vacuo. Yield: 90.5 mg, 97%. ^1H NMR (CD_2Cl_2): δ = 1.23 and 1.31 (s each, 18H each, ^{t}Bu-CH_3), 1.75 (s, 4H, NBD-CH_2), 2.58 (s, 6H, Py-CH_3), 3.62 (d, 4H, Ar-CH_2, J = 13.1 Hz), 4.37 (m, 8H, Ar-CH_2 and NBD-CH), 4.66 (s, 8H, NBD-CH-olefins), 5.23 (s, 4H, Py-CH_2-OR), 7.21 (s, 8H, Ar H), 7.47 (d, 2H, Py H, J = 5.4 Hz), 7.58 (d, 2H, Py H, J = 5.2 Hz), 7.66 (d, 2H, Py H, J = 5.4 Hz), 7.72 (d, 2H, Py H, J = 5.1 Hz), 7.89 (s, 2H, Py H), 8.28 (s, 2H, Ar-OH), 9.15 (s, 2H, Py H) ppm. ^{13}C NMR (CD_2Cl_2): δ = 22.26 (Py-CH$_3$), 31.23 (^{t}BuCH$_3$), 31.64 (^{t}BuCH$_3$), 32.39 (ArCH$_2$), 34.20 (^{t}BuC), 34.64 (^{t}BuC), 52.92 (NBDCH), 64.35 (d, NBDCH$_2$, J = 2.3 Hz), 64.60 (d, NBDCH-olefins), 75.80 (PyCH$_3$-OR), 119.55 (Py-CH of pyCH$_2$), 123.63 (Py-CH of pyCH$_3$), 124.86 (Py-CH of pyCH$_2$), 127.09 (ArCH), 127.32 (ArC-OH), 129.49 (PyCH of pyCH$_3$), 132.64 (ArC-OR), 143.98 (ArC-^{t}Bu), 148.75 (ArC-CH$_2$ of Ar-OH), 148.94 (PyCH of pyCH$_3$), 149.71 (ArC-^{t}Bu of Ar-OR), 150.02 (ArC-CH$_2$ of Ar-OR), 150.20 (PyCH of PyCH$_2$), 151.99 (PyC-CH$_2$),

---

[16] Green, M.; Kuc, T. A.; Taylor, S. H. *J. Chem. Soc. A* **1971**, 2334−2337.

154.10 (Py*C*-CH$_3$), 154.92 (Py*C*-C of PyCH$_3$), 156.19 (Py*C*-C of pyCH$_2$) ppm. ^{15}N NMR (CD$_3$OD): $\delta = 203.00$ (d, 2N, ^2J and ^3J with Py H, $^2J_{\mathrm{N,Rh}} = 19.8$ Hz), 208.30 (d, 2N, ^2J and ^3J with py H, $^2J_{\mathrm{N,Rh}} = 20.0$ Hz) ppm. Anal. Calcd for $C_{82}H_{92}B_2F_8N_4O_4Rh_2$ (M_r = 1577.16): C, 62.45; H, 5.88; N, 3.55. Found: C, 62.36; H, 5.76; N, 3.47.

Preparation of BBPC[PdCl$_2$]$_2$ (5). An orange solution of PdCl$_2$(CH$_3$CN)$_2$ (21.0 mg, 0.081 mmol) in CH$_2$Cl$_2$ (8 mL) was added to a solution of BBPC (**3**) (40 mg, 0.040 mmol) in CH$_2$Cl$_2$ (2 mL). The resulting yellow solution was stirred at room temperature for 3 h, during which time a pale yellow precipitate formed. The precipitate was filtered off, washed with dichloromethane and diethyl ether, and dried in vacuo. Yield: 53.0 mg, 96%. ^{1}H NMR (C$_5$D$_5$N): $\delta = 0.79$ and 1.44 (s each, 18H each, ^{t}Bu-C*H*$_3$), 2.13 (s, 6H, Py-C*H*$_3$), 3.66 (d, 4H, Ar-C*H*$_2$, $J = 13.0$ Hz), 4.63 (d, 4H, Ar-C*H*$_2$, $J = 12.9$ Hz), 5.14 (s, 4H, Py-C*H*$_2$-OR), 6.98 (d, 2H, Py *H*, $J = 4.9$ Hz), 7.09 (s, 4H, Ar *H*), 7.46 (s, 4H, Ar *H*), 8.22 (d, 2H, Py *H*, $J = 5.0$ Hz), 8.53 (s, br, 2H, Py *H*), 8.58 (d, 2H, Py *H*, $J = 4.9$ Hz), 8.74 (d, 2H, Py *H*, $J = 5.0$ Hz), 8.84 (s, 2H, Ar-O*H*), 8.92 (s, 2H, Py *H*) ppm. Anal. Calcd for $C_{68}H_{76}Cl_4N_4O_4Pd_2$ (M_r = 1368.06): C, 59.70; H, 5.60; N, 4.10. Found: C, 59.67; H, 5.69; N, 4.03.

Preparation of BBPC[NiBr$_2$]$_2$ (6). NiBr$_2$(DME) (62.0 mg, 0.198 mmol) in CH$_2$Cl$_2$ (2 mL) was added to a solution of the ligand BBPC (100.0 mg, 0.099 mmol) in CH$_2$Cl$_2$ (5 mL), and the resulting mixture was stirred at room temperature for 48 h. Evaporation of the solvent gave a pale green solid, which was washed with diethyl ether and dried in vacuo. Yield: 130.0 mg, 91%. Anal. Calcd for $C_{68}H_{76}Br_4N_4O_4Ni_2$ (M_r = 1450.50): C, 56.31; H, 5.29; N, 3.86. Found: C, 56.24; H, 5.31; N, 3.94. Because of the paramagnetic nature of the compound, NMR peaks are broad and shifted. Assignments are tentative. The compound is sparingly soluble at room temperature and dissolved upon mild heating. NMR of the warm solution was measured. ^{1}H NMR (CDCl$_3$): $\delta = -9.77$ (br s, 2H, Py *H*), -1.95 (br s, 2H, Py *H*), 0.06 (s, 4H, Py-C*H*$_2$-OR), 0.89 (br s 6H, Py-C*H*$_3$), 1.19 (s, 18H, ^{t}Bu-C*H*$_3$), 1.44 (s, 18H, ^{t}-Bu-C*H*$_3$), 1.27 (br s, overlapped, 2H, Py *H*), 3.39 (br s, 4H, Ar-C*H*$_2$), 3.55 (s, 4H, Ar-C*H*$_2$), 3.86 (br s 2H, Py *H*), 4.74 (br s 2H, Py *H*), 5.31 (br s, 2H, Py *H*), 7.12 (bs, 4H, Ar *H*), 7.47 (br s, 4H, Ar *H*), 8.65 (br s, 2H, Ar-O*H*). UV/vis (CHCl$_3$): λ (ϵ) 284 (54 600), 295 (66 200), 304 (64 000).

Preparation of BBPC[NiBr(OCH$_3$)] (7). Complex **6** (31.0 mg, 0.021 mmol) was dissolved in methanol (3 mL), and the solution was concentrated by slow evaporation at room temperature forming yellow crystals of **7** in low (ca. 10%) yield. ^{1}H NMR (in CDCl$_3$) of this paramagnetic compound exhibited very broad, difficult to assign peaks in the range of -15 to $+10$ ppm. UV/vis. (MeOH): λ (ϵ) 293 (28 800), 305 (26 400).

X-ray Crystal Structure Determination of 4, 5, and 7. Single crystals of **4, 5,** and **7** were mounted on the nylon loop in cryooil and flash frozen in a nitrogen stream at 120 K. Data were collected on a Nonius KappaCCD diffractometer mounted on a FR590 generator equipped with a sealed tube with Mo Kα radiation (λ = 0.710 73 Å) and a graphite monochromator. The structures were solved using direct methods with SHELXS-97 and refined by the full-matrix least-squares technique with SHELXL-97 based on F^2.[17]

Complex 4: $C_{82}H_{92}N_4O_4Rh_2 + 2\ BF_4 + CH_3CN + 2\ CH_2Cl_2$; orange, needles, 0.30 × 0.05 × 0.03 mm^3; orthorhombic, *Pbca* (No. 61); $a = 15.191(3)$, $b = 23.208(5)$, $c = 47.149(9)$ Å, from 10 deg of data; $V = 16623(6)$ Å^3, $Z = 8$; fw = 1787.94; $D_c = 1.429$ Mg/m^3; $\mu = 0.597$ m^{-1}. The final cycle of refinement based on F^2 gave an agreement factor $R = 0.0743$ for data with $I > 2\sigma(I)$ and $R = 0.0873$ for all data (4892 reflections) with a goodness-of-fit of 1.022. Idealized hydrogen atoms were placed and refined in a riding mode.

Complex 5: $C_{68}H_{76}Cl_4N_4O_4Pd_2 + 5\ O{=}C(CH_3)_2]$; yellow, needles, 0.20 × 0.10 × 0.10 mm^3; triclinic, $P\bar{1}$; $a = 11.805(2)$, $b = 26.644(5)$, $c = 28.186(9)$ Å; $\alpha = 65.820(3)$, $\beta = 84.540(10)$, $\gamma = 85.420(10)°$; $V = 8043(4)$ Å^3, $Z = 2$; fw = 1658.32; $D_c = 1.370$ Mg/m^3; $\mu = 0.638$ mm^{-1}. The final cycle of refinement based on F^2 gave an agreement factor $R = 0.0488$ for data with $I > 2\sigma(I)$ and $R = 0.0635$ for all data (18 953 reflections) with a goodness-of-fit of 1.030. Idealized hydrogen atoms were placed and refined in a riding mode.

Complex 7: $C_{69}H_{77}N_4O_5NiBr + HBr + 7\ CH_3OH$; green, plates, 0.20 × 0.20 × 0.05 mm^3; triclinic, $P\bar{1}$ (No. 2); $a = 11.8697(2)$, $b = 15.3304(4)$, $c = 22.4468(6)$ Å; $\alpha = 87.071(1)$, $\beta = 87.604(2)$, $\gamma = 74.615(2)°$; $V = 3931.4(2)$ Å^3, $Z = 2$; fw = 822.46; $D_c = 1.281$ Mg/m^3; $\mu = 1.324$ mm^{-1}. The final cycle of refinement based on F^2 gave an agreement factor $R = 0.056$ for data with $I > 2\sigma(I)$ and $R = 0.062$ for all data (10 724 reflections) with a goodness-of-fit of 1.074. Idealized hydrogen atoms were placed and refined in a riding mode.

Acknowledgment. This work was supported by the Israel Science Foundation, Jerusalem, Israel, and by the MINERVA Foundation, Munich, Germany. We thank Ishai Sher and Shlomit Davidzon (Graphics Department, WIS) for producing the cover picture. D.M. is the Israel Matz Professor of Organic Chemistry.

Supporting Information Available: Tables of crystal and structure refinement data, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for complexes **4**, **5**, and **7** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC020643A

---

[17] Sheldrick, G. M. *SHELX-97, Program for Crystal Structure Refinement*; University of Goettingen: Goettingen, Germany, 1997.