3516 *Organometallics* **2005,** *24,* 3516−3526

Supermolecular Assembly of Tetra- and Hexanuclear Carbonyl Clusters Using a Novel Polydentate Pyridylphosphine Ligand

Igor O. Koshevoy,[†,‡] Matti Haukka,[‡] Tapani A. Pakkanen,[*,‡]
Sergey P. Tunik,[*,†] and Pirjo Vainiotalo[‡]

*Department of Chemistry, St. Petersburg State University, Universitetskii pr., 26,
St. Petersburg 198504, Russian Federation, and Department of Chemistry, University of
Joensuu, P.O. Box 111, FIN-80101 Joensuu, Finland*

Received March 18, 2005

The novel heterodentate ligand 2,2′-bis(diphenylphosphino)-4,4′-bipyridine (dpbp, **1**) was synthesized and spectroscopically characterized. The reaction of **1** with 2 equiv of [Rh$_6$(CO)$_{15}$(NCMe)] or [Ru$_6$C(CO)$_{17}$] afforded the linked double-homometallic clusters [{Rh$_6$(CO)$_{14}$}$_2$dpbp] (**2**) and [{Ru$_6$C(CO)$_{15}$}$_2$dpbp] (**3**), respectively, where **1** is coordinated to the hexanuclear metal cores in a P,N bridging mode. Treatment of [Ru$_6$C(CO)$_{17}$] with an excess of dpbp results in formation of the complex [Ru$_6$C(CO)$_{15}$dpbp] (**4**) to leave a phosphinopyridyl functionality uncoordinated. The heterocluster double compounds [Ru$_6$C(CO)$_{15}$dpbpRh$_6$(CO)$_{14}$] (**5**) and [Ru$_6$C(CO)$_{15}$dpbpIr$_4$(CO)$_{10}$] (**7**) were obtained by the reactions of **4** with [Rh$_6$(CO)$_{15}$(NCMe)] and [Ir$_4$(CO)$_{11}$Br][NBu$_4$]. The mixed-valence complex [{Ru$_6$C(CO)$_{15}$(dpbp)}$_2$Rh$^{I}_{2}$(CO)Cl$_2$] (**6**) was synthesized via the interaction of 2 equiv of **4** with the dimer [Rh$_2$(CO)$_4$Cl$_2$]. The tri- and tetracluster compounds {Ru$_6$C(CO)$_{15}$(dpbp)}$_2$Ir$_4$(CO)$_{10}$ (**8**) and {Ru$_6$C(CO)$_{15}$(dpbp)}$_3$Ir$_4$(CO)$_8$ (**10**) were prepared by treatment of **7** with 1 or 2 equiv of **4**, respectively. Cluster **8** appears to be unstable toward loss of one CO ligand and formation of {Ru$_6$C(CO)$_{15}$(dpbp)}$_2$Ir$_4$(CO)$_9$ (**9**), where one {Ru$_6$C(CO)$_{15}$dpbp} unit is coordinated to the tetrairidium framework in a κ^1 mode through the phosphorus atom and another {Ru$_6$C(CO)$_{15}$dpbp} fragment in a P,N bridging mode. The structures of **2**, **3**, and **5** were established by X-ray crystallography and by ESI$^+$ mass and ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. The other supermolecular complexes **4** and **6**−**10** were characterized by spectroscopic methods.

Introduction

Synthesis of high-nuclearity clusters and cluster-containing molecules of high molecular weight with well-defined composition and structure is a challenging task that attracts significant attention stimulated by a number of purely academic and practical reasons. Specific structural features of transition-metal clusters and their “electron buffer ability” allow making use of the cluster complexes as versatile building blocks for the synthesis of complicated molecular networks, macromolecules and nanosized materials, which could find various applications in nanoelectronics, nonlinear optics, sensors, etc.[1−4] The architecture of the desired molecules and materials may be constructed and their properties may be tuned up by the design ligand environment of the cluster complexes. In this respect bridging polyfunctional ligands connecting the cluster fragments and also serving as spacers, which determine the electronic connection inside the network, play particularly important roles.

The clusters linked by bridging ligands have been receiving considerable attention over the past 15 years. Most of the reported structures contain various functionalized organic molecules[5−9] or phosphines as linking groups between the metal subunits.[10−16] It is worth

---

[*] To whom correspondence should be addressed. E-mail: stunik@chem.spbu.ru (S.P.T.); Tapani.Pakkanen@joensuu.fi (T.A.P.).

[†] St. Petersburg State University.

[‡] University of Joensuu.

(1) Braunstein, P. *J. Organomet. Chem.* **2004**, *689*, 3953.

(2) Ichikawa, M. In *Metal Clusters in Chemistry*; Braunstein, P., Oro, L. A., Raithby, P. R., Eds.; Wiley-VCH: Weinheim, Germany, 1999; Vol. 3, p 1273.

(3) Johnson, B. F. G. *Coord. Chem. Rev.* **1999**, *190−192*, 1269.

(4) Schweyer-Tihay, F.; Braunstein, P.; Estournes, C.; Guille, J. L.; Lebeau, B.; Paillaud, J.-L.; Richard-Plouet, M.; Rose, J. *Chem. Mater.* **2003**, *15*, 57.

(5) Deeming, A. J. *J. Cluster Sci.* **1992**, *3*, 347.

(6) Ainscough, E. W.; Brodie, A. M.; Coll, R. K.; Kotch, T. G.; Lees, A. J.; Mair, A. J. A.; Waters, J. M. *J. Organomet. Chem.* **1996**, *517*, 173.

(7) Zhang, J.; Chen, X.-N.; Yin, Y.-Q.; Wang, W.-L.; Huang, X.-Y. *J. Organomet. Chem.* **1999**, *582*, 252.

(8) Torma, V.; Vidoni, O.; Simon, U.; Schmid, G. *Eur. J. Inorg. Chem.* **2003**, 1121.

(9) Song, L.-C.; Zhu, W.-F.; Hua, Q.-M.; Wua, H.; Yu, G.-A. *J. Organomet. Chem.* **2003**, *667*, 143.

(10) Amoroso, A. J.; Johnson, B. F. G.; Lewis, J.; Massey, A. D.; Raithby, P. R.; Wong, W. T. *J. Organomet. Chem.* **1992**, *440*, 219.

(11) Amoroso, A. J.; Edwards, A. J.; Johnson, B. F. G.; Lewis, J.; Al-Mandhary, M. R.; Raithby, P. R.; Saharan, V. P.; Wong, W. T. *J. Organomet. Chem.* **1993**, *443*, C11.

(12) Adams, C. J.; Bruce, M. I.; Horn, E.; Skelton, B. W.; Tiekink, E. R. T.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1993**, 3299.

(13) Housecroft, C. E.; Rheingold, A. L.; Waller, A.; Yap, G. P. A. *J. Organomet. Chem.* **1998**, *565*, 105.

(14) Ferrer, M.; Julia, A.; Rossell, O.; Seco, M.; Pellinghelli, M. A.; Tiripicchio, A., *Organometalics* **1997**, *16*, 3715.

(15) Imhof, D.; Burckhardt, U.; Dahmen, K.-H.; Joho, F.; Nesper, R. *Inorg. Chem.* **1997**, *36*, 1813.

(16) Feeder, N.; Geng, J.; Goh, P. G.; Johnson, B. F. G.; Martin, C. M.; Shephard, D. S.; Zhou, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 1661.

10.1021/om0502032 CCC: \$30.25

stressing that the number of complexes where three or more carbonyl cluster fragments are linked by the phosphines is still very limited.[10,14–17] Relatively slow progress in this field is very probably determined by the lack of appropriate and easily available ligands, which could be used for the design of supermolecular arrays. In this respect the functionalized 4,4′-bipyridine and related ligands could provide an effective route to diverse organometallic supermolecular complexes. The use of relatively hard aromatic N-donor ligands in most cases favors their complexation to the metal centers in positive oxidation states.[18–20] The reported carbonyl cluster complexes containing nonlabile N-heteroaryl moieties normally display additional supporting metal-to-ligand interactions such as, for example, ortho-metalated M–C bonds[21–24] and M–N[25–27] or M–P[28–31] dative bonds. Therefore, the functionalization of the 4,4′-bipyridine molecule (i.e. introduction of the additional coordinating group, which can be more strongly bonded to a cluster core) could significantly expand the coordination chemistry of this class of ligands. In the present paper we report the synthesis of the novel heteropolydentate diphosphine 2,2′-bis(diphenylphosphino)-4,4′-bipyridine and its coordination chemistry with tetranuclear iridium and hexanuclear rhodium and ruthenium clusters.

Experimental Section

General Comments. 2,2′-Dibromo-4,4′-bipyridine,[32] Ph_2PLi,[33] $Rh_6(CO)_{15}NCMe$,[34] $Rh_2(CO)_4Cl_2$,[35] $Ru_6C(CO)_{17}$,[36] and $[Ir_4(CO)_{11}Br][NBu_4]$[37] were synthesized according to published procedures. Reagent grade solvents—acetonitrile, dichloromethane, diethyl ether, toluene, methanol, hexane, and toluene—were used as received. Tetrahydrofuran was distilled over Na–benzophenone ketyl under a nitrogen atmosphere prior to use. The products were purified by column chromatography on silica (5–40 mesh, Merck Kieselgel 60). Mass spectra (for compounds **1**–**3** and **5**–**10**) were determined on a Bruker BioAPEX II 47e FT-ICR instrument, using the ESI$^+$ routine. The IR spectra were recorded on a Nicolet 550 Magna FTIR spectrophotometer. Microanalyses were carried out in the Analytical Laboratory of the University of Joensuu. The solution ^1H and ^{31}P NMR spectra were recorded on Bruker Avance 250, Bruker DPX 300, and Bruker Avance 400 spectrometers. The chemical shifts were referenced to residual solvent resonances and external 85% H_3PO_4 in the ^1H, ^{13}C, and ^{31}P spectra, respectively.

2,2′-Bis(diphenylphosphino)-4,4′-bipyridine (dpbp, 1). A solution of 2,2′-dibromo-4,4′-dipyridine (2.66 g, 8.47 mmol) in THF (30 cm^3) was added dropwise over a period of 30 min to a cooled (−70 °C) solution of PPh_2Li in THF (50 cm^3) prepared from PPh_2Cl (3.7 cm^3) and Li (0.4 g). The cooling bath was then removed, and the dark reaction mixture was warmed to room temperature. The mixture was stirred for 4 h and concentrated under reduced pressure to ca. 20 cm^3. A degassed 3 N aqueous solution of HCl (40 cm^3) was added to the solution obtained. The organic solvent was removed in vacuo, and the solution was filtered, thoroughly washed with Et_2O (5 × 30 cm^3), and basified with a degassed saturated aqueous solution of Na_2CO_3. Washing with ether removes some of the impurities, and basification leads to precipitation of the crude product. The dark amorphous precipitate was washed with water and vacuum-dried. It was extracted with CH_2Cl_2 (3 × 5 cm^3), leaving some gray insoluble material, and purified using column chromatography on silica (silica for column chromatography, 3.5 × 7 cm, eluant CH_2Cl_2/Et_2O (15/1, v/v)). The solvent was removed, and the resulting yellow material was recrystallized from CH_2Cl_2/hexane under a nitrogen atmosphere to give a crystalline solid of white to slightly yellowish color (1.64 g, 37%). ES MS (*m/z*): [M$^+$] 524 (calcd 524). $^{31}P\{^1H\}$ NMR ($CDCl_3$; δ): −2.8 (s). ^1H NMR ($CDCl_3$; δ): 8.76 (d, Py, 1H, J(H–H) = 4.9 Hz), 7.38 (m, Ph, 10H), 7.20 (m, Py, 2H). Anal. Calcd for $C_{34}H_{26}N_2P_2$: C, 77.85; H, 5.0; N, 5.34. Found: C, 77.35; H, 4.97; N, 5.34.

$\{Rh_6(CO)_{14}\}_2$dpbp (2). A twofold excess of $Rh_6(CO)_{15}NCMe$ (80 mg, 0.074 mmol) and 1 equiv of dpbp (19 mg, 0.036 mmol) were dissolved in degassed CH_2Cl_2 (10 cm^3) under N_2, and the reaction mixture was stirred for 1 h at room temperature. It was then carefully heated (ca. 40 °C) for 3 h until a TLC spot test showed formation of one major product and complete disappearance of intermediate complexes with higher R_f. The solvent was removed in vacuo to give almost black material, which was suspended in CH_2Cl_2 (2 cm^3) and the suspension diluted with hexanes (1.5 cm^3) and filtered. The precipitate, which contains mainly **2**, was dissolved in CH_2Cl_2 (ca. 15 cm^3) and purified by flash chromatography on silica (column 2 × 2 cm) using CH_2Cl_2 as eluent. The filtrate was diluted with CH_2Cl_2 (0.5 cm^3) and transferred onto a chromatographic column (2.5 × 8 cm). Elution with a CH_2Cl_2/hexane (5/3, v/v) mixture gave one main dark brown broad band of **2**. Combined fractions of **2** were dried in vacuo to give a dark brown microcrystalline product (73 mg, 78%). IR (CH_2Cl_2; ν(CO)/cm^{-1}): 2090 m, 2060 s, 2046 sh, 2028 m, 2004 w, 1776 m, br. ES MS (*m/z*): [(M + Na)$^+$] 2566 (calcd 2566). $^{31}P\{^1H\}$ NMR (CD_2Cl_2; δ): 25.3 (ddm, ^1J(P–Rh) = 147 Hz, ^2J(P–Rh) = 17 Hz). ^1H NMR (CD_2Cl_2; δ): 9.28 (dm, Py, 1H, J(H–H) = 5.7 Hz), 7.57–7.33 (m, Ph, Py, 11H), 7.16 (m, Py, 1H). Anal. Calcd for $Rh_{12}C_{62}H_{26}N_2O_{28}P_2\cdot CH_2Cl_2$: C, 28.79; H, 1.07; N, 1.07. Found: C, 28.73; H, 1.22; N, 1.06.

Single crystals of **2** suitable for X-ray analysis were grown by gas-phase diffusion of hexane into a CH_2Cl_2/CH_3OH solution under a nitrogen atmosphere at room temperature.

$\{Ru_6C(CO)_{15}\}_2$dpbp (3). Two equivalents of $Ru_6C(CO)_{17}$ (41 mg, 0.037 mmol) and 1 equiv of dpbp (9.5 mg, 0.018 mmol) were dissolved in degassed CH_2Cl_2 (15 cm^3) under N_2, and the reaction mixture was stirred for 2 h at room temperature. The solvent was removed in vacuo to give almost black material,

---

(17) Geng, J.; Li, H.; Huck, W. T. S.; Johnson, B. F. G. *Chem. Commun.* **2004**, 2122.

(18) Togni, A.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 7.

(19) Chelucci, G.; Thummel, R. P. *Chem. Rev.* **2002**, *102*, 3129.

(20) Kaes, C.; Katz, A.; Hosseini, M. W. *Chem. Rev.* **2000**, *100*, 3553.

(21) Deeming, A. J.; Peters, R.; Hursthouse, M. B.; Backer-Dirks, J. D. J. *J. Chem. Soc., Dalton Trans.* **1982**, 787.

(22) Foulds, G. A.; Johnson, B. F. G.; Lewis, J. *J. Organomet. Chem.* **1985**, *294*, 123.

(23) Wong, W. Y.; Cheung, S. H.; Lee, S. M.; Leung, S. Y. *J. Organomet. Chem.* **2000**, *596*, 36.

(24) Wong, W.-Y.; Cheung, S.-H.; Huang, X.; Lin, Z. *J. Organomet. Chem.* **2002**, *655*, 39.

(25) Chan, S.; Wong, W. T. *J. Chem. Soc., Dalton Trans.* **1994**, 1605.

(26) Ros, R.; Bertani, R.; Tassan, A.; Braga, D.; Grepioni, F.; Tedesco, E. *Inorg. Chim. Acta* **1996**, *244*, 11.

(27) Freeman, G.; Ingham, S. L.; Johnsopn, B. F. G.; McPartlin, M.; Scowen, I. J. *J. Chem. Soc., Dalton Trans.* **1997**, 2705.

(28) Tunik, S. P.; Koshevoy, I. O.; Poe, A. J.; Farrar, D. H.; Nordlander, E.; Haukka, M.; Pakkanen, T. A. *Dalton* **2003**, 2457.

(29) Wajda-Hermanowicz, K.; Pruchnik, F.; Zuber, M. *J. Organomet. Chem.* **1996**, *508*, 75.

(30) Deeming, A. J.; Smith, M. B. *J. Chem. Soc., Dalton Trans.* **1993**, 3383.

(31) Ponomarenko, V. I.; Pilyugina, T. S.; Khripun, V. D.; Grachova, E. V.; Tunik, S. P.; Haukka, M.; Pakkanen, T. A. *Eur. J. Inorg. Chem.*, in press.

(32) Kelly, T. R.; Lee, Y.-J.; Mears, R. J. *J. Org. Chem.* **1997**, *62*, 2774.

(33) Newkome, G. R.; Hager, D. C. *J. Org. Chem.* **1978**, *43*, 947.

(34) Tunik, S. P.; Vlasov, A. V.; Krivykh, V. V. *Inorg. Synth.* **1997**, *31*, 239.

(35) McCleverty, J. A.; Wilkinson, G. *Inorg. Synth.* **1966**, *8*, 211.

(36) Braga, D.; Grepioni, F.; Dyson, P. J.; Johnson, B. F. G.; Frediani, P.; Bianchi, M.; Piacenti, F. *J. Chem. Soc., Dalton Trans.* **1992**, 2565.

(37) Chini, P.; Ciani, G.; Garlaschelli, L.; Manassero, M.; Martinengo, S.; Sironi, A.; Canziani, F. *J. Organomet. Chem.* **1978**, *152*, C35.

which was suspended in CH_2Cl_2 (2 cm^3), diluted with hexanes (1.5 cm^3), and filtered. The precipitate, which contains mainly **3**, was dissolved in CH_2Cl_2 (ca. 10 cm^3) and passed through the flash column (2 × 2 cm) using CH_2Cl_2 as eluant. The filtrate was diluted with CH_2Cl_2 (0.5 cm^3) and transferred onto a chromatographic column (2.5 × 8 cm). Elution with a CH_2Cl_2/hexane (5/3, v/v) mixture gave trace amounts of unreacted $Ru_6C(CO)_{17}$ and main dark brown broad band of **3**. The combined samples of **3** were dried in vacuo to give dark brown microcrystalline product (36 mg, 76%). IR (CH_2Cl_2; ν(CO)/cm^{-1}): 2072 m, 2032 sh, 2024 s, 2004 sh, 1966 w, 1819 vw. ES MS (*m/z*): [M^+] 2602 (calcd 2602). $^{31}P\{^1H\}$ NMR (CD_2Cl_2; δ): 26.4 (s). ^1H NMR (CD_2Cl_2; δ): 9.34 (dm, Py, 1H, *J*(H−H) = 6.1 Hz), 7.58−7.27 (m, Ph, Py, 11H), 6.91 (dm, Py, 1H, *J*(H−P) = 5.1 Hz). Anal. Calcd for $Ru_{12}C_{66}H_{26}N_2O_{30}P_2 \cdot CH_2Cl_2$: C, 29.95; H, 1.05; N, 1.04. Found: C, 30.07; H, 1.34; N, 1.06. Single crystals of **3** suitable for X-ray analysis were grown by slow diffusion of hexane into a CH_2Cl_2 solution at room temperature.

$Ru_6C(CO)_{15}$(dpbp) (4). $Ru_6C(CO)_{17}$ (71 mg, 0.065 mmol) and excess dpbp (86 mg, 0.164 mmol) were dissolved in degassed CH_2Cl_2 (20 cm^3) under a nitrogen atmosphere, and the solution was stirred at room temperature for 40 min until a TLC spot test showed complete consumption of the starting $Ru_6C(CO)_{17}$ cluster. The resulting dark red-brown reaction mixture was concentrated under reduced pressure to ca. 4 mL, diluted with hexane (0.4 cm^3), and transferred onto a chromatographic column (2.5 × 6 cm). Elution with CH_2Cl_2/hexane (12/1, v/v) mixture gave small amounts of **3**, a main dark brown broad band of **4**, and trace amounts of unidentified complexes. The band containing **4** was concentrated, diluted with hexane to cause precipitation of the brown product, and dried in vacuo (74 mg, 73%). The cluster **4** is unstable both in solution and in the solid state and was used in subsequent chemistry immediately after preparation. IR (CH_2Cl_2; ν(CO)/cm^{-1}): 2071 m, 2029 sh, 2021 s, 2001 sh, 1965 w, 1818 vw. $^{31}P\{^1H\}$ NMR (CD_2Cl_2; δ): 25.9 (s, 1P), −2.2 (s, 1P). ^1H NMR (CD_2Cl_2; δ): 9.26 (d, Py, 1H, *J*(H−H) = 6.0 Hz), 8.80 (d, Py, 1H, *J*(H−H) = 5.0 Hz), 7.63−7.34 (m, Ph, Py, 21H), 7.18 (dm, Py, 1H, *J*(H−P) = 5.1 Hz), 7.12 (m, Py, 2H).

$Ru_6C(CO)_{15}(dpbp)Rh_6(CO)_{14}$ (5). A solution of **4** (55 mg, 0.035 mmol) in degassed CH_2Cl_2 (5 cm^3) was added to $Rh_6(CO)_{15}$(NCMe) (40 mg, 0.037 mmol) in degassed CH_2Cl_2 (5 cm^3) under a nitrogen atmosphere, and the reaction mixture was stirred overnight at room temperature. It was stirred for an additional 2 h at slightly elevated temperature (40 °C). The solvent was then removed, and the resulting oily material was dissolved in CH_2Cl_2 (2.5 cm^3), diluted with hexane (1.5 cm^3), and transferred onto a chromatographic column (2.5 × 7 cm). Elution with a CH_2Cl_2/hexane (5/3, v/v) mixture gave the main brown band of **5** (74 mg, 82%) and small amounts of an unidentified complex with lower R_f. IR (CH_2Cl_2; ν(CO)/cm^{-1}): 2091 m, 2072 m, 2059 s, 2026 s, 2004 sh, 1966 w, 1818 vw, 1778 w, br. ES MS (*m/z*): [M^+] 2573 (calcd 2573). $^{31}P\{^1H\}$ NMR (CD_2Cl_2; δ): 26.3 (s, 1P), 24.8 (dm, 1P, ^1J(P−Rh) = 145 Hz). ^1H NMR (CD_2Cl_2; δ): 9.31 (m, Py, 2H), 7.61−7.27 (m, Ph, Py, 22H), 7.17 (dd, Py, 1H, *J*(H−P) = 2.8 Hz, *J*(H−H) = 2.4 Hz), 6.92 (dd, Py, 1H, *J*(H−P) = 4.7 Hz, *J*(H−H) = 1.9 Hz). Anal. Calcd for $Ru_6Rh_6C_{64}H_{26}N_2O_{29}P_2$: C, 29.88; H, 1.02; N, 1.09. Found: C, 29.88; H, 1.31; N, 1.08. Single crystals of **5** suitable for X-ray analysis were grown by gas-phase diffusion of hexane into a $CH_2Cl_2-C_2H_5OH$ solution under a nitrogen atmosphere at room temperature.

$\{Ru_6C(CO)_{15}(dpbp)\}_2Rh_2(CO)Cl_2$ (6). A solution of **4** (70 mg, 0.045 mmol) in degassed CH_2Cl_2 (5 cm^3) was added to crystalline $Rh_2(CO)_4Cl_2$ (9.5 mg, 0.024 mmol) under a nitrogen atmosphere. The reaction mixture was stirred for 30 min, reduced in volume to ca. 2 cm^3, and diluted with degassed Et_2O (10 cm^3). The pale mother liquor was decanted, and the brown amorphous precipitate was washed with ether (2 × 5 cm^3) and dried in vacuo to give 68 mg (81%) of **6**. IR (CH_2Cl_2; ν(CO)/cm^{-1}): 2072 m, 2031 sh, 2022 s, 2003 sh, 1966 w, 1814 vw. ES MS (*m/z*): [M^+] 3432 (calcd 3432). $^{31}P\{^1H\}$ NMR (CD_2Cl_2; δ): 45.5 (dm, 1P, *J*(P−Rh) = 139 Hz), 26.3 (s, 1P). ^1H NMR (CD_2Cl_2; δ): 9.35 (dm, Py, 1H, *J*(H−H) = 5.2 Hz), 9.29 (d, Py, 1H, *J*(H−H) = 6.0 Hz), 7.61−7.28 (m, Ph, Py, 22H), 6.98 (m, Py, 2H). Anal. Calcd for $Ru_{12}Rh_2C_{101}H_{52}N_4O_{31}P_4Cl_2$: C, 35.36; H, 1.53; N, 1.63. Found: C, 35.16; H, 1.65; N, 1.59.

$Ru_6C(CO)_{15}(dpbp)Ir_4(CO)_{10}$ (7). A solution of **4** (69 mg, 0.044 mmol) in degassed CH_2Cl_2 (10 mL) was added dropwise over a period of 20 min to a cooled (−20 °C) solution of $[Ir_4(CO)_{11}Br][NBu_4]$ (51 mg, 0.036 mmol) in degassed CH_2Cl_2 (5 mL) under a nitrogen atmosphere. The reaction mixture was stirred at ca. −10 °C for 1 h. The reaction mixture was warmed to room temperature and concentrated under reduced pressure to ca. 3 cm^3. It was then diluted with hexane (1.5 cm^3) and transferred onto a chromatographic column (2.5 × 8 cm). Elution with a CH_2Cl_2/hexane (2/1, v/v) mixture gave the main brown band of **7** (59 mg, 62%) and small amounts of **8**. IR (CH_2Cl_2; ν(CO)/cm^{-1}): 2088 w, 2081 w, 2072 m, 2057 m, 2041 m, 2031 sh, 2022 s, 2001 sh, 1969 w, 1841 vw, 1820 vw. ES MS (*m/z*): [(M + Na)$^+$] 2635.5 (calcd 2636). $^{31}P\{^1H\}$ NMR ($CDCl_3$; δ): isomer **a** 26.4 (s, 1P), −14.8 (s, br, 1P); isomer **b** 26.3 (s, 1P), −44.0 (s, br, 1P). ^1H NMR (CD_2Cl_2; δ): 9.27 (isomers **a** and **b**, d, Py, *J*(H−H) = 6.1 Hz), 9.21 (**b**, d, Py, *J*(H−H) = 6.0 Hz), 8.79 (**a**, d, Py, *J*(H−H) = 5.1 Hz), 7.66−7.25 (**a** and **b**, m, Ph, Py), 7.18 (**b**, dt, Py, *J*(H−H) = 5.9 Hz, *J*(H−P) = 2.0 Hz), 7.09−7.03 (m, Ph), 7.01 (**a**, dd, Py, *J*(H−H) = 2.0 Hz, *J*(H−P) = 4.8 Hz), 6.96 (**a**, dm, Py, *J*(H−P) = 4.5 Hz), 6.81 (**b**, dd, Py, *J*(H−H) = 2.1 Hz, *J*(H−P) = 4.8 Hz), 6.70 (**b**, dd, Py, *J*(H−H) = 2.1 Hz, *J*(H−P) = 4.1 Hz). Anal. Calcd for $Ru_6Ir_4C_{60}H_{26}N_2O_{25}P_2$: C, 27.59; H, 1.00; N, 1.07. Found: C, 27.64; H, 1.20; N, 1.08.

$\{Ru_6C(CO)_{15}(dpbp)\}_2Ir_4(CO)_{10}$ (8). Method A. A solution of **4** (110 mg, 0.07 mmol) in degassed CH_2Cl_2 (15 mL) was added dropwise over a period of 30 min to a cooled (−20 °C) solution of $[Ir_4(CO)_{11}Br][NBu_4]$ (39 mg, 0.028 mmol) in degassed CH_2Cl_2 (5 mL) under a nitrogen atmosphere. The cooling bath was then removed, and the reaction mixture was stirred overnight at room temperature. The solution was concentrated to ca. 3 cm^3, diluted with hexane (1.5 cm^3), and transferred onto a chromatographic column (2.5 × 8 cm). Elution with a CH_2Cl_2/hexane (5/2, v/v) mixture gave the main brown band of **8** (93 mg, 80%) and trace amounts of **7** and **9**. IR (CH_2Cl_2; ν(CO)/cm^{-1}): 2071 m, 2041 sh, 2032 sh, 2021 s, 2003 sh, 1966 w, 1821 w br, 1797 vw. ES MS (*m/z*): [M^+] 4176 (calcd 4176). $^{31}P\{^1H\}$ NMR (CD_2Cl_2; δ): 28.1 (unresolved m, 2P), 16.4 (s, br, 1P), −14.0 (s, br, 1P). ^1H NMR (CD_2Cl_2; δ): 9.26 (d, Py, 1H, *J*(H−H) = 6.0 Hz), 8.83 (d, Py, 1H, *J*(H−H) = 4.9 Hz), 7.76−7.35 (m, Ph, Py, 21H), 7.24 (m, Py, 1H), 7.13 (m, Py, 1H), 7.09 (dd, Py, 1H, *J*(H−P) = 4.8 Hz, *J*(H−H) = 2.1 Hz). Anal. Calcd for $Ru_{12}Ir_4C_{110}H_{52}N_4O_{40}P_4 \cdot C_6H_{14}$: C, 32.69; H, 1.56; N, 1.31. Found: C, 32.44; H, 1.54; N, 1.31.

Method B. A solution of **4** (38 mg, 0.024 mmol) in degassed CH_2Cl_2 (10 cm^3) was added to **7** (43 mg, 0.016 mmol, in 5 cm^3 of CH_2Cl_2), and the reaction mixture was stirred overnight at room temperature. The product was separated in the same manner as described in method **A**, to give 51 mg (74%) of **8**.

$\{Ru_6C(CO)_{15}(dpbp)\}_2Ir_4(CO)_9$ (9). A solution of **8** (56 mg, 0.013 mmol) in degassed CH_2Cl_2 (15 cm^3) was gently refluxed under nitrogen for 20 h. The solution obtained was then concentrated to ca. 3 cm^3, diluted with hexane (1.5 cm^3), and transferred onto a chromatographic column (2.5 × 8 cm). Elution with a CH_2Cl_2/hexane (5/2, v/v) mixture gave the main brown band of **9** (50 mg, 90%) and small amounts of unidentified complexes. IR (CH_2Cl_2; ν(CO)/cm^{-1}): 2072 m, 2051 sh, 2030 sh, 2021 s, 2000 sh, 1965 sh, 1817 w br, 1785 vw. ES MS (*m/z*): [M^+] 4148 (calcd 4148). $^{31}P\{^1H\}$ NMR ($CDCl_3$; δ): isomers **a** and **b** 26.6−26.3 (m), −8.6 (s), −13.1 (s), −15.3 (s, br), −15.7 (s, br). ^1H NMR (CD_2Cl_2; δ): 9.27 (isomers **a** and **b**, m, Py), 8.77 (**a**, m, Py), 8.69 (**b**, d, Py, *J*(H−H) = 5.7 Hz), 7.59−7.32 (**a** and **b**, m, Ph, Py), 7.21 (**a**, m, Py), 7.14 (**a**, m, Py), 7.04

Table 1. Crystal Data and Structure Refinement for 2, 3, and 5

	2	**3**	**5**
empirical formula	$C_{65}H_{32}Cl_6N_2O_{28}P_2Rh_{12}$	$C_{66}H_{26}N_2O_{30}P_2Ru_{12}$	$C_{74.5}H_{50}Cl_3N_2O_{29}P_2Rh_6Ru_6$
formula wt	2798.49	2601.67	2829.33
temp, K	120(2)	120(2)	120(2)
wavelength, Å	0.710 73	0.710 73	0.710 73
cryst syst	orthorhombic	triclinic	monoclinic
space group	$C222_1$	$P\bar{1}$	$P2_1/c$
unit cell dimens			
a, Å	16.700(3)	9.9103(6)	30.9444(4)
b, Å	23.066(5)	12.8948(8)	17.9287(2)
c, Å	21.127(4)	14.9814(10)	35.4368(5)
α, deg	90	89.197(4)	90
β, deg	90	89.266(5)	114.522(5)
γ, deg	90	71.650(4)	90
V, Å^3	8138(3)	1816.9(2)	17886.8(4)
Z	4	1	8
calcd density, Mg/m^3	2.284	2.378	2.101
abs coeff, mm^{-1}	2.678	2.548	2.259
goodness of fit on F^2	1.045	1.056	1.084
final R indices ($I > 2\sigma(I)$)	R1 = 0.0311, wR2 = 0.0643	R1 = 0.0464, wR2 = 0.1063	R1 = 0.0530, wR2 = 0.1326
R indices (all data)	R1 = 0.0387, wR2 = 0.0674	R1 = 0.0787, wR2 = 0.1216	R1 = 0.0754, wR2 = 0.1462

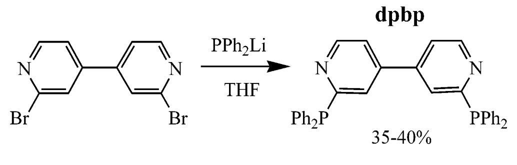
(**b**, m, Py), 6.95 (**a**, m, Py), 6.50 (**b**, dm, Py, J(H−P) = 4.9 Hz). Anal. Calcd for $Ru_{12}Ir_4C_{109}H_{52}N_4O_{39}P_4$: C, 31.57; H, 1.26; N, 1.35. Found: C, 31.53; H, 1.48; N, 1.34.

$\{Ru_6C(CO)_{15}(dpbp)\}_3Ir_4(CO)_8$ (10). A solution of **4** (41 mg, 0.026 mmol) in degassed CH_2Cl_2 (10 cm^3) was added under nitrogen to **9** (75 mg, 0.018 mmol, 10 cm^3 in degassed CH_2Cl_2), and the reaction mixture was stirred overnight at room temperature. The solution obtained was gently refluxed for 10 h under a nitrogen atmosphere, cooled, concentrated to ca. 4 cm^3, diluted with hexane (0.5 cm^3), and transferred onto a chromatographic column (2.5 × 9 cm). Elution with a CH_2Cl_2/hexane (12/1, v/v) mixture gave the main brown band of **10** and small amounts of unidentified complexes. The band containing **10** was concentrated to ca. 2 cm^3 and slowly diluted with hexane (8 cm^3) to cause precipitation of a brown amorphous material. The mother liquor was decanted; the product was washed with hexane and vacuum-dried to give 71 mg (69%) of **10**. IR (CH_2Cl_2; ν(CO)/cm^{-1}): 2071 m, 2031 sh, 2020 s, 2002 sh, 1968 w, 1816 vw, 1794 vw, 1771 vw. ES MS (m/z): [M$^+$] 5682 (calcd 5684). ^{31}P{^{1}H} NMR (CD_2Cl_2; δ): 29.9 (dd, 1P, ^3J(P−P) = 47.9 Hz, ^3J(P−P) = ca. 2 Hz), 28.3 (s, 1P), 28.1 (s, 1P), 27.9 (s, 1P), −8.7 (dd, 1P, ^3J(P−P) = 47.9 Hz, ^3J(P−P) = 2.7 Hz), −11.9 (t, 1P, ^3J(P−P) = 2.4 Hz). ^{1}H NMR (CD_2Cl_2; δ): 9.24 (m, Py, 3H), 8.79 (d, Py, 1H, J(H−H) = 4.8 Hz), 8.64 (d, Py, 1H, J(H−H) = 5.2 Hz), 8.56 (d, Py, 1H, J(H−H) = 5.6 Hz), 7.73 (m, Py, 2H), 7.59−7.09 (m, Ph, Py, 67H), 7.01 (dm, Py, 1H, J(H−P) = 5.6 Hz), 6.97 (dd, Py, 1H, J(H−P) = 4.7 Hz, J(H−H) = 2.1 Hz), 6.50 (dd, Py, 1H, J(H−P) = 4.1 Hz, J(H−H) = 2.0 Hz). Anal. Calcd for $Ru_{18}Ir_4C_{158}H_{78}N_6O_{53}P_6 \cdot C_6H_{14}$: C, 34.15; H, 1.61; N, 1.46. Found: C, 34.39; H, 1.62; N, 1.48.

X-ray Structure Determinations. The X-ray diffraction data were collected with a Nonius KappaCCD diffractometer using Mo Kα radiation (λ = 0.710 73 Å). Single crystals of **2**, **3**, and **5** were mounted in inert oil in the cold gas stream of the diffractometer. The Denzo-Scalepack[38] program package was used for cell refinements and data reduction. Structures were solved by direct methods using the SHELXS-97 and SIR-97 programs.[39,40] A multiscan absorption correction based on equivalent reflections (XPREP in SHELXTL v. 6.14)[41] was applied to all data (T_{min}/T_{max} values were 0.11919/0.15877, 0.18727/0.23721, and 0.4330/0.8329 for **2**, **3**, and **5**). All structures were refined with SHELXL-97[42] and a WinGX graphical user interface.[43] The structure **2** was refined in the noncentrosymmetric space group $C222_1$. The absolute configuration was determined by refining the Flack parameter. The structure **2** contained two disordered CH_2Cl_2 molecules in the asymmetric unit. These solvent molecules were refined isotropically with a constant C−Cl distance of 1.75 Å. Furthermore, one of the Cl atoms was refined over two positions with equal occupancies. Hydrogens of the CH_2Cl_2 molecules were omitted. The asymmetric unit of **5** consists of two Ru_6−Rh_6 moieties and three dichloromethane and three hexane molecules. One of the CH_2Cl_2 molecules is disordered over two positions with occupation factors of ca. 0.52/048. One of the hexanes is disordered over three sites, with an occupancy of $^1/_3$. Two atoms in the second hexane were also disordered over two sites with equal occupancies. Atoms in all disordered solvents were located from the difference Fourier map but not refined. The carbon atoms of the third hexane molecule were refined with equal U_{iso} values. The crystallographic data are summarized in Table 1, and selected bond lengths and angles are given in the figure captions.

Results and Discussion

Synthesis of the dpbp Ligand and Its Reactions with Hexanuclear Rhodium and Ruthenium Clusters. The one-step synthesis affords a novel ligand (2,2′-bis(diphenylphosphino)-4,4′-bipyridine; dpbp, **1**) in a moderate yield. The reaction was carried out in a manner commonly used[33,44] to obtain a number of pyridyldiphenylphosphine ligands. The ligand contains four donor functionalities: two pyridyl nitrogens and two phosphorus atoms. The architecture of **1** allows for a rich coordination chemistry of this diphosphine in polynuclear complexes: first, due



---

[38] Otwinowski, Z.; Minor, W. *Macromolecular Crystallography*; Methods in Enzymology 276; Carter, J. C. W., Sweet, R. M., Eds.; Academic Press: London, 1997; Part A, p 307.

[39] Sheldrick, G. M. SHELXS97, Program for Crystal Structure Determination; University of Göttingen, Göttingen, Germany, 1997.

[40] Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. J. *J. Appl. Crystallogr.* **1999**, *32*, 115.

[41] Sheldrick, G. M. SHELXTL, version 6.14; Bruker Analytical X-ray Systems, Madison, WI, 2003.

[42] Sheldrick, G. M. SHELXL97, Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1997.

[43] Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

[44] Spencer, L. P.; Altwer, R.; Wei, P.; Gelmini, L.; Gauld, J.; Stephan, D. W. *Organometallics* **2003**, *22*, 3841.

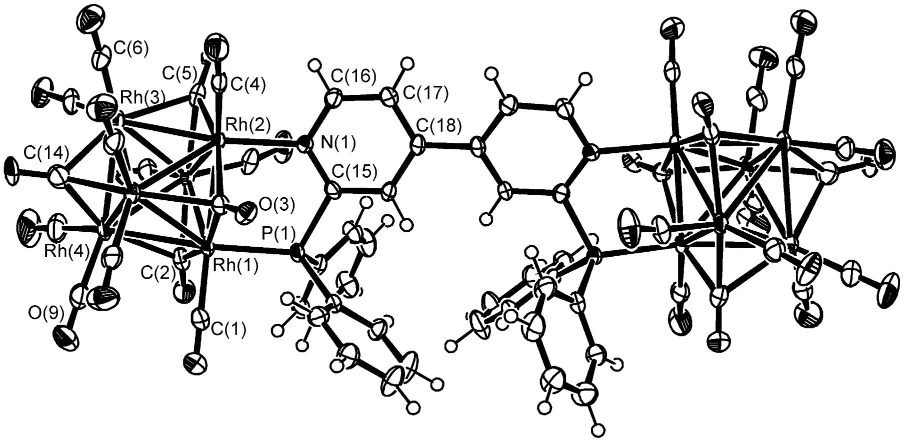


Figure 1. ORTEP plot of the molecular structure of [$Rh_6(CO)_{14}\{\mu,\kappa^2:\mu,\kappa^2$-dpbp$\}Rh_6(CO)_{14}$] (**2**). Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): average Rh−Rh = 2.7504(276); Rh(1)−P(1) = 2.2733(14); Rh(2)−N(1) = 2.179(4); average Rh-μ_3-CO = 2.185(71); average Rh−CO_t = 1.897(28); P(1)−Rh(1)−Rh(2) = 89.43(4); N(1)−Rh(2)−Rh(1) = 92.41(10); P(1)−Rh(1)−Rh(5) = 98.20(4); N(1)−Rh(2)−Rh(5) = 100.40(10).

to variations in bonding of an individual 2-pyridylphosphine moiety,[29,30,45−48] and second, due to easy visible opportunity to tag together two metal (polymetal) fragments. The composition of **1** was established by elemental analysis, mass spectroscopic data, and ^1H NMR spectroscopy, and the structure shown above was later confirmed by the crystallographic analysis of the complexes formed in the reactions of **1** with hexanuclear clusters of rhodium and ruthenium. The ligand can be isolated in an analytically pure state only under anaerobic conditions; otherwise, it contains a minor amount of the phosphine oxide contaminations. This moderate sensitivity to oxidation by air is quite typical for the majority of pyridylphosphines.[33,49]

The reaction of [$Rh_6(CO)_{15}(NCMe)$] with P-donor ligands has previously been used for the synthesis of a wide range of monosubstituted [$Rh_6(CO)_{15}PR_3$][50] and disubstituted [$Rh_6(CO)_{14}(\mu$-PX)] (PX = heterobidentate phosphines)[28,51] derivatives, which were completely characterized by various spectroscopic methods and X-ray crystallography. A similar reaction of 2 equiv of the labile [$Rh_6(CO)_{15}(NCMe)$] cluster with **1** followed by gentle heating of the reaction mixture affords the dimeric substituted complex [$Rh_6(CO)_{14}\{\mu,\kappa^2:\mu,\kappa^2$-dpbp$\}$-$Rh_6(CO)_{14}$] (**2**) in good yield. Both 2-pyridylphosphine moieties of the ligand are coordinated to the Rh_6 cluster cores in a bridging manner to form five-membered dimetallacycles similar to the previously described [$Rh_6(CO)_{14}(PPh_2$(2-pyridyl))] substituted derivatives.[28] The solid-state structure of **2** has been determined by X-ray crystallography. An ORTEP view of this molecule is shown in Figure 1; selected structural parameters are given in the figure caption.

The structural characteristics of **2** are closely analogous to those found earlier for the similar substituted clusters mentioned above. The principal bond lengths and averages for the $\{Rh_6(CO)_{14}\}$ fragment of **2** fall in the range found earlier for these compounds.[28,51,52] The orientation of the coordinated pyridyl rings with respect to the Rh−N bond and the parameters of the dimetallacycles are also similar to those in the [$Rh_6(CO)_{14}\{\mu,\kappa^2$-$Ph_2P$(pyridyl)$\}$] cluster.[28] The dihedral angle formed by the planes of the pyridyl rings in **2** is 156.8°, which is quite close to the values revealed in the polymetallic complexes bridged by 4,4′-dipyridine: 166.3° in [$Os_3(\mu$-$H)(CO)_{10}(\mu$-$NC_5H_3C_5H_3N)Os_3(\mu$-$H)(CO)_{10}$] and 145.2° in [$Os_3(\mu$-$H)(CO)_{10}(\mu$-$NC_5H_3C_5H_4N)W(CO)_5$].[24] The spectroscopic data obtained for **2** (IR, ^1H, ^{31}P NMR) show that the structure found in the solid state remains unchanged in solution. The $^{31}P\{^1H\}$ NMR spectrum of **2** displays a doublet at 25.3 ppm (ddm, ^1J(P−Rh) = 147 Hz, ^2J(P−Rh) = 17 Hz) that points to the equivalence of the phosphorus atoms and also to their coordination to the $\{Rh_6\}$ cores. The typical low-field shift of the H^6 ($H^{6\prime}$) signal in the proton spectrum of **2** compared to the shift for the free ligand (8.76 ppm in **1**; cf. 9.28 ppm in **2**) is indicative of the pyridyl functionality coordination revealed in the solid state.

The reaction of 2 equiv of the [$Ru_6C(CO)_{17}$] cluster with **1** occurs spontaneously at room temperature to give the double cluster [$Ru_6C(CO)_{15}\{\mu,\kappa^2:\mu,\kappa^2$-dpbp$\}$-$Ru_6C(CO)_{15}$] (**3**) in good yield. The easy substitution of carbonyl ligands in the [$Ru_6C(CO)_{17}$] cluster by mono-[53−55] and diphosphines[56−58] is well documented. However, to the best of our knowledge there are no examples of functionalized heterobidentate phosphines coordinting to this cluster either in bridging or in chelating positions. The only related structure reported in the

---

(45) Farr, J. P.; Olmstead, M. M.; Hunt, C. H.; Balch, A. L. *Inorg. Chem.* **1981**, *20*, 1182.

(46) Kuang, S.-M.; Fanwick, P. E.; Walton, R. A. *Inorg. Chim. Acta* **2000**, *305*, 102−105.

(47) Suzuki, T.; Kuchiyama, T.; Kishi, S.; Kaizaki, S.; Kato, M. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 2433−2439.

(48) Zhang, Z. Z.; Cheng, H. *Coord. Chem. Rev.* **1996**, *147*, 1.

(49) Newkome, G. R. *Chem. Rev.* **1993**, *93*, 2067.

(50) Farrar, D. H.; Grachova, E. V.; Lough, A.; Patirana, C.; Poe, A. J.; Tunik, S. P. *Dalton* **2001**, 2015.

(51) Babij, C.; Browning, C. S.; Farrar, D., H.; Koshevoy, I. O.; Podkorytov, I. S.; Poe, A. J.; Tunik, S. P. *J. Am. Chem. Soc.* **2002**, *124*, 8922.

(52) Farrar, D. H.; Grachova, E. V.; Haukka, M.; Heaton, B. T.; Iggo, J. A.; Pakkanen, T. A.; Podkorytov, I. S.; Tunik, S. P. *Inorg. Chim. Acta* **2003**, *354*, 11.

(53) Johnson, B. F. G.; Lewis, J.; Wong, K.; McPartlin, M. *J. Organomet. Chem.* **1980**, *185*, C17.

(54) Brown, S. C.; Evans, J.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1981**, 2263.

(55) Adams, R. D.; Captain, B.; Fu, W.; Smith, M. D. *J. Organomet. Chem.* **2002**, *651*, 124.

(56) Gracey, B. P.; Evans, J.; Jones, A. G.; Webster, M. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1987**, *C43*, 2286.

(57) Blake, A. J.; Harrison, A.; Johnson, B. F. G.; McInnes, E. J. L.; Parsons, S.; Shephard, D. S.; Yellowlees, L. J. *Organometallics* **1995**, *14*, 3160.

(58) Adatia, T.; Conole, G.; Drake, S. R.; Johnson, B. F. G.; Kessler, M.; Lewis, J.; McPartin, M. *J. Chem. Soc., Dalton Trans.* **1997**, 669.

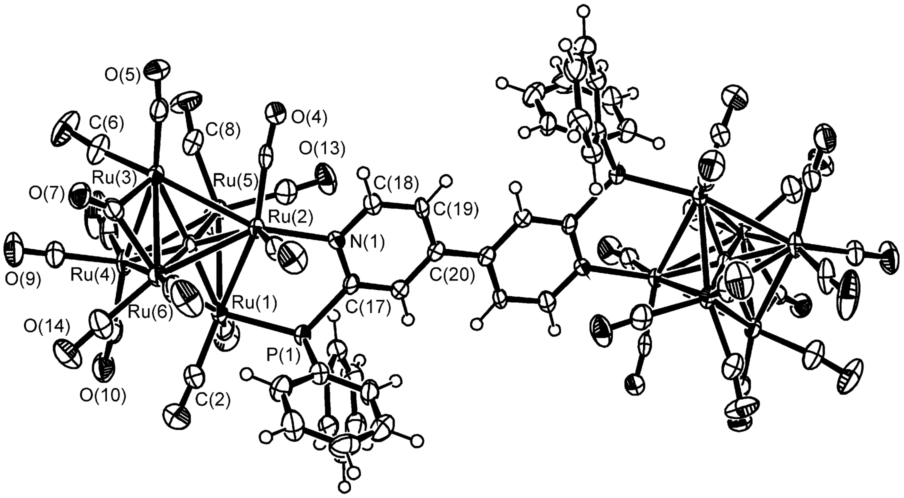


Figure 2. ORTEP plot of the molecular structure of $[Ru_6C(CO)_{15}\{\mu,\kappa^2{:}\mu,\kappa^2\text{-dpbp}\}Ru_6C(CO)_{15}]$ (**3**). Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): average Ru−Ru = 2.8964(439); Ru(1)−P(1) = 2.286(2); Ru(2)−N(1) = 2.154(6); average Ru-μ_2-CO = 2.098(67); average Ru−CO_t = 1.897(28); average Ru-μ_6-C = 2.049(21); P(1)−Ru(1)−Ru(2) = 76.88(6); N(1)−Ru(2)−Ru(1) = 94.83(17); P(1)−Ru(1)−Ru(5) = 108.47(6); N(1)−Ru(2)−Ru(5) = 98.50(17).

literature contains the arylphosphines coordinated to the $\{Ru_6C\}$ framework through the phosphorus atom and a phenyl ring, which substitutes three CO ligands in a η^6 manner.[59,60] This observation demonstrates the strong tendency of the hexanuclear ruthenium framework to form η^6-arene complexes.[61,62] Therefore, **3** is the first example of a hexaruthenium cluster bearing a bridging heterobidentate phosphine ligand. The solid-state structure of **3** has been determined by X-ray crystallography. An ORTEP view of this molecule is shown in Figure 2; selected structural parameters are given in the figure caption.

The dpbp ligand is coordinated to the both $\{Ru_6\}$ cores in a bridging mode, similar to that observed for the $\{Rh_6\}$ analogue. The $\{Ru_6C\}$ framework of the parent cluster remains intact, and the phosphino-pyridyl moieties of **1** substitute two terminal carbonyl groups at adjacent ruthenium atoms to form the five-membered dimetallacycle with a nonplanar N(1)Ru(2)Ru(1)P(1) fragment. The corresponding torsion angle equals 24.0°, which is very close to the value found for the P−Ru−Ru−P fragment in the $[Ru_6C(CO)_{15}(dppe)]$ cluster.[58] This nonplanarity of the dimetallacycle presumably reflects the orientation of available vacancies at these ruthenium atoms that is also indicated by similar dihedral angles for the (O)C−Ru−Ru−C(O) systems (22.7 and 32.1°) in the parent $[Ru_6C(CO)_{17}]$ cluster.[36] Both cluster moieties in **3** possess slightly asymmetric bridging carbonyl ligands (Ru(3)−C(7) = 2.146(9) Å, Ru(6)−C(7) = 2.051(9) Å) that is similar to the case for related $[Ru_6C(CO)_{15}(\text{diphosphine})]$ clusters.[58] The Ru−Ru bond distances (the average is 2.8964 Å) fall in the interval typical for disubstituted carbidoruthenium analogues.[58,62] The Ru(1)−P(1) bond (2.286(2) Å) is slightly shorter than those found for other $\{Ru_6C\}$ phosphine derivatives (e.g., 2.340(3)−2.365(8) Å for $[Ru_6C(CO)_{15}(\text{diphosphine})]$[58] and 2.359(3) Å for $[Ru_6C(CO)_{16}(PPh_2Et)]$[54]). The Ru(2)−N(1) bond length (2.154(6) Å) is not exceptional and correlates with values found for the other pyridylphosphine-containing ruthenium complexes.[31,63] The metal−carbide distances are nearly equal to each other within experimental uncertainty and fall in the range observed for related structures.[58,62] In contrast to the case for **2**, the pyridyl rings in **3** are coplanar. The IR and ^1H and ^{31}P NMR spectral data recorded for **3** show that the structure found in the solid state remains unchanged in solution. The $^{31}P\{^1H\}$ NMR spectrum displays a singlet at 26.4 ppm, which points to symmetrical coordination of dpbp to both hexaruthenium cluster cores. The ^1H NMR spectrum resembles closely that of **2**, indicating the bidentate P,N coordination mode of each pyridylphosphine moiety.

The reaction of **1** with a threefold excess of $[Ru_6C(CO)_{17}]$ affords $[Ru_6C(CO)_{15}\{\mu,\kappa^2\text{-dpbp}\}]$ (**4**) as the main product in very good yield (up to 75%). The availability of **4**, which has free pyridylphosphine functionality, allows for the synthesis of mixed-metal complexes containing different cluster moieties. For example, the reaction between **4** and $[Rh_6(CO)_{15}(NCMe)]$ affords initially $[Ru_6C(CO)_{15}\{\mu,\kappa^2{:}\kappa^1\text{-dpbp}\}Rh_6(CO)_{15}]$ (**5a**), where **1** is coordinated to the $\{Rh_6\}$ core in a κ^1 mode through the phosphorus atom. This intermediate complex was detected by IR spectroscopy. The instability of **5a** toward P,N bridge closure prevented the complete characterization of this compound. Gentle heating of **5a** under anaerobic conditions resulted in nearly quantitive loss of one CO ligand to form the stable $[Ru_6C(CO)_{15}\{\mu,\kappa^2{:}\mu,\kappa^2\text{-dpbp}\}Rh_6(CO)_{15}]$ cluster (**5**). This stepwise coordination of the pyridylphosphine function to the hexarhodium cluster was described in detail earlier.[28] The solid-state structure of **5** has been determined by X-ray crystallography. An ORTEP view of this molecule is shown in Figure 3. Two independent molecules have been found in the unit cell of **5**; they are essentially

---

(59) Hsu, H. F.; Wilson, S. R.; Shapley, J. R. *Organometallics* **1997**, *16*, 4937.

(60) Phillips, G.; Hermans, S.; Adams, J. R.; Johnson, B. F. G. *Inorg. Chim. Acta* **2003**, *352*, 110.

(61) Ma, L.; Williams, G. K.; Shapley, J. R. *Coord. Chem. Rev.* **1993**, *128*, 261.

(62) Braga, D.; Dyson, P. J.; Grepioni, F.; Johnson, B. F. G. *Chem. Rev.* **1994**, *94*, 1585.

(63) Field, J. S.; Haines, R. J.; Parry, C. J. *J. Chem. Soc., Dalton Trans.* **1997**, 2843.

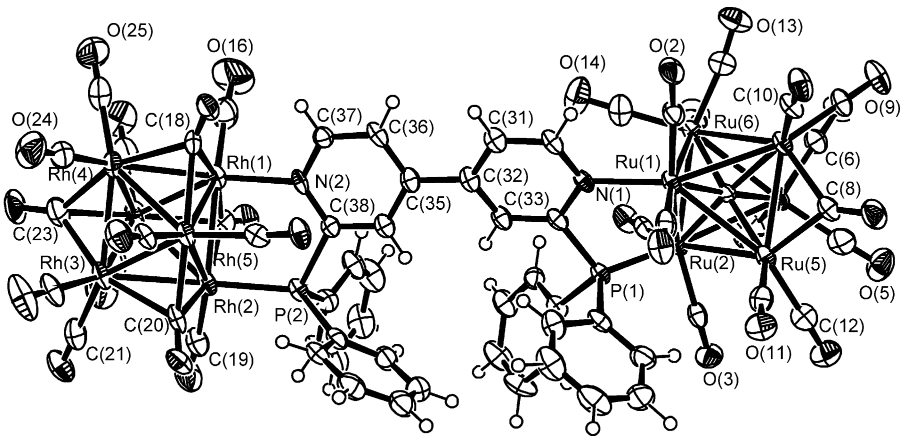
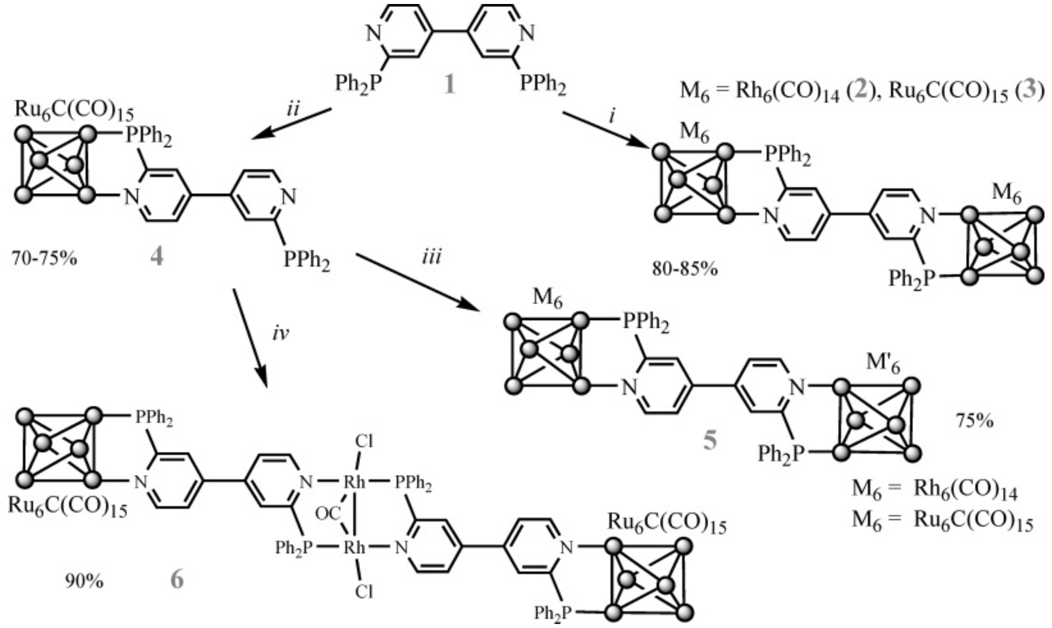


Figure 3. ORTEP plot of the molecular structure of $[Ru_6C(CO)_{15}\{\mu,\kappa^2:\mu,\kappa^2\text{-dpbp}\}Rh_6(CO)_{14}]$ (**5**). Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): average Ru−Ru = 2.9029(594); Ru(2)−P(1) = 2.290(2); Ru(1)−N(1) = 2.143(7); average Ru−μ_2-CO = 2.058(17); average Ru−CO$_t$ = 1.897(16); average Ru−μ_6-C = 2.053(25); average Rh−Rh = 2.7476(324); Rh(2)−P(2) = 2.295(2); Rh(1)−N(2) = 2.144(7); average Rh−μ_3-CO = 2.196(54); average Rh−CO$_t$ = 1.897(14); P(1)−Ru(2)−Ru(1) = 75.17(6); N(1)−Ru(1)−Ru(2) = 92.08(18); P(1)−Ru(2)−Ru(5) = 106.48(6); N(1)−Ru(1)−Ru(5) = 141.39(19); P(2)−Rh(2)−Rh(1) = 89.33(7); N(2)−Rh(1)−Rh(2) = 92.4(2); P(2)−Rh(2)−Rh(5) = 100.84(6); N(2)−Rh(1)−Rh(5) = 92.04(19).

Scheme 1[a]



[a] Legend: (i) 2 equiv of $Rh_6(CO)_{15}(NCMe)$ or $Ru_6C(CO)_{17}$; (ii) $^1/_3$ equiv of $Ru_6C(CO)_{17}$; (iii) 1 equiv of $Rh_6(CO)_{15}(NCMe)$; (iv) 0.5 equiv of $Rh_2(CO)_4Cl_2$.

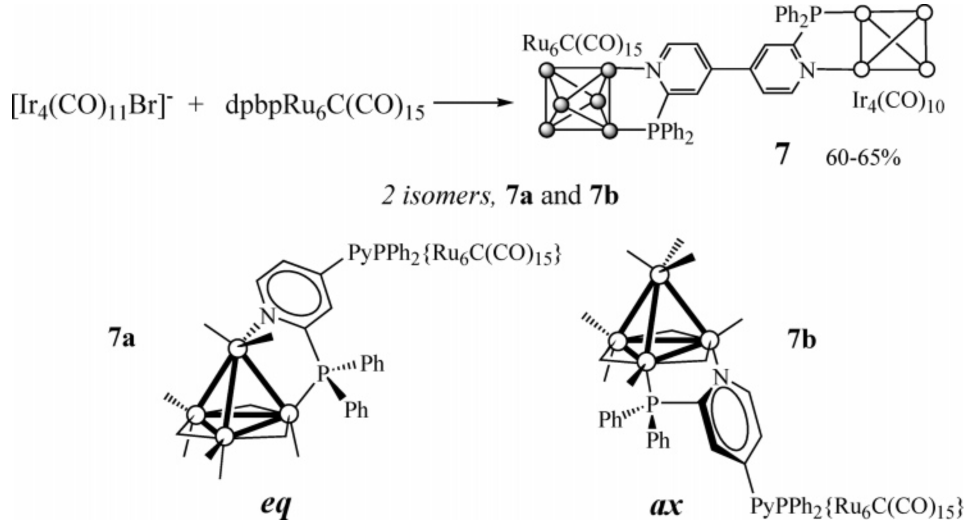
similar and display only minor variations in bond lengths and angles.

The dpbp ligand is coordinated in a bridging P,N manner to both the $\{Ru_6C\}$ and $\{Rh_6\}$ cluster frameworks. The structures of both cluster fragments are closely analogous to those observed for the "homocluster" species **2** and **3**. The torsion angle between the planes of pyridyl rings in **5** equals 161.8°, which is very close to the average of the values found for **2** and **3**. The IR and ^1H and ^{31}P NMR spectroscopic patterns obtained for **5** look like superimposition of the corresponding spectra recorded for the rhodium (**2**) and ruthenium (**3**) compounds. In particular, the $^{31}P\{^1H\}$ NMR spectrum displays two signals of equal intensities at 26.3 (s) and 28.8 ppm (dm, $^1J(P-Rh) = 145$ Hz), which confirms the coordination of the dpbp ligand at ruthenium and rhodium cluster cores. The coordination shift of H^6 and $H^{6\prime}$ nuclei in the proton spectrum indicates the bridging bidentate P,N coordination of both pyridylphosphine functionalities. These observations clearly indicate that in solution the cluster **5** retains the structure revealed in the solid state.

Treatment of the rhodium dimer $[Rh_2(CO)_4Cl_2]$ with 2 equiv of **4** resulted in nearly quantitive formation of the mixed tricluster compound $[(Ru_6C(CO)_{15}\{\mu,\kappa^2:\mu,\kappa^2\text{-dpbp}\})_2Rh_2(\mu\text{-CO})Cl_2]$ (**6**) (Scheme 1).

This complex did not give crystals suitable for X-ray analysis, and its structure was established on the basis of spectroscopic data. Its ESI mass spectrum displays a molecular ion signal at *m/z* 3432 that completely fits the stoichiometry given above. As expected, the IR spectrum of **6** in the carbonyl region closely resembles those of **3** and **4**, and a nonresolved band of bridging CO located on the dirhodium moiety is very probably masked by the absorption of bridging carbonyls of the hexaruthenium fragments. The ^1H NMR spectrum

Scheme 2



displays two well-resolved low-field signals of the H^6 and $H^{6'}$ protons (9.35 and 9.29 ppm) corresponding to the pyridyl rings bound to different (ruthenium and rhodium) metal centers. The $^{31}P\{^1H\}$ NMR spectrum of **6** shows a multiplet (45.5 ppm, $^1J(P-Rh) = 139$ Hz) and a singlet (26.3 ppm) of equal intensity. The low-field signal should be assigned to the AA′XX′ spin system (A = P, X = Rh), and its fine structure matches very well the previously described pattern for the complex $[Rh_2(Ph_2PPy)_2(CO)Cl_2]$ (44.18 ppm, $^1J(P-Rh) = 144.0$ Hz).[45] The structure of this signal corresponds to a head-to-tail coordination mode of the $\{Ru_6C(CO)_{15}dpbp\}$ units to the $\{Rh_2\}$ fragment. The high-field singlet should be assigned to the phosphorus atoms bound to the hexaruthenium cores. These spectral features fit completely the structure of **6** shown in Scheme 1. The effective synthesis of **6** demonstrates the possibility to combine in one molecule a few metal centers in different oxidation states that in principle could provide a route to compounds and/or materials which possess unusual physicochemical properties.

Heterocluster Ruthenium−Iridium Complexes. It has been shown earlier that $[Ir_4(CO)_{12}]$ can accommodate up to three 2-pyridylphosphines on its metal framework upon substitution of the carbonyl ligands.[29,64] This well-developed chemistry of the tetrahedral iridium cluster together with successful synthesis of the heterometallic compounds **5** and **6** inspired us to use the complex **4** for the preparation of mixed metal Ir−Ru supermolecules. We investigated the reactions of **4** with $[Ir_4(CO)_{11}Br][NBu_4]$ with intention to tie up the Ir_4 and a few Ru_6 fragments.

Treatment of $[Ir_4(CO)_{11}Br][NBu_4]$ with a small excess of **4** in a dichloromethane solution afforded $[Ru_6C(CO)_{15}\{\mu,\kappa^2:\mu,\kappa^2\text{-dpbp}\}Ir_4(CO)_{10}]$ (**7**) in good yield (60−65%). The structure of this compound was established on the basis of the IR, mass, and NMR spectroscopic data. The ESI mass spectrum of **7** diplays a signal at *m/z* 2635.5 corresponding to $(M + Na)^+$ ion (calcd 2636), and its isotopic distribution pattern perfectly fits the calculated one. The $^{31}P\{^1H\}$ spectrum consists of two groups of signals. The first one, low-field shifted, shows two closely disposed singlets (26.4 and 26.3 ppm, relative intensities ca. 1.5/1, respectively). These signals can be assigned to the phosphorus atoms bound to the $\{Ru_6\}$ clusters. The second group displays two broadened signals (−14.8 and −44.0 ppm) of similar relative intensities that are associated with the phosphorus atoms bound to the $\{Ir_4\}$ cores. This spectral pattern could be explained in terms of the presence of two isomers (Scheme 2), each of which contains the phosphorus atom coordinated at a basal iridium center in either an axial or an equatorial position.

The broadening of the high-field resonances is most probably a result of the isomerization/carbonyl scrambling processes, which are typical for the phosphine-substituted $\{Ir_4\}$ clusters.[65−68] The ^1H NMR spectroscopic data (^1H (Figure 4), $^1H-^1H$ COSY spectra (Figure S1; the prefix “S” indicates that the figure is available in the Supporting Information) obtained for **7** are also consistent with the structure proposed in Scheme 2 and confirm the presence of two isomers in solution. The combination of 1D and 2D routines together with the reported data on the pyridylphosphine-substituted iridium clusters[29] allows complete assignment of the ^1H spectrum, as shown in the upper part of Figure 4.

As expected, the room-temperature spectrum shows three signals between 9.3 and 8.70 ppm (9.27 ppm, $J(H-H) = 6.1$ Hz; 9.21 ppm, $J(H-H) = 6.0$ Hz; 8.79 ppm, $J(H-H) = 5.1$ Hz) of relative intensities 2.2/1/1.2. These resonances have been assigned to the hydrogen atoms in the 6- and 6′-positions of two nonequivalent bipyridyl fragments bound to ruthenium and iridium cluster cores, respectively. The low-field signal is a combination of nonresolved H^6 resonances associated with the ruthenium clusters. Overlapping of these signals is evidently due to the lower effect of the $\{Ir_4\}$-related isomerism on the $\{Ru_6\}$-bonded pyridyl fragments, whereas the signals of $\{Ir_4\}$-bound pyridyl protons are well separated in the spectrum. The reso-

---

(64) Arena, C. G.; Drommi, D.; Faraone, F.; Lanfranchi, M.; Nicolo, F.; Tiripicchio, A. *Organometallics* **1996**, *15*, 3170.

(65) Besancon, K.; Laurenczy, G.; Lumini, T.; Roulet, R.; Gervasio, G. *Helv. Chim. Acta* **1993**, *76*, 2926.

(66) Strawczynski, A.; Suardi, G.; Ros, R.; Roulet, R. *Helv. Chim. Acta* **1993**, *76*, 2210.

(67) Strawczynski, A.; Hall, C.; Bondietti, G.; Ros, R.; Roulet, R. *Helv. Chim. Acta* **1994**, *77*, 754.

(68) Roulet, R. *NATO ASI Ser., Ser. C* **1995**, *465*, 159.

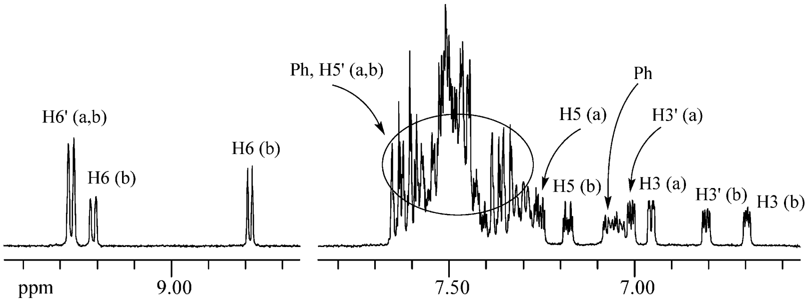
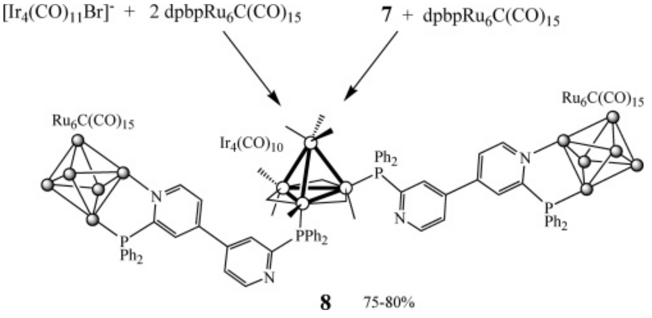


Figure 4. 400 MHz ^{1}H spectrum of **7** (CD_2Cl_2, 293 K).

Scheme 3



nances of the isomers **7a** and **7b** may be tentatively distinguished on the basis of their comparison with the proton NMR spectrum of $[Ir_4(CO)_8(\mu\text{-}PPh_2Py)(PPh_2Py)_2]$.[29] In this cluster the signal of the H^6 nucleus of the bridging pyridyl ring appears at 8.49 ppm, which is close to the highest field doublet (8.79 ppm) in the spectrum of **7** and allows association of the latter resonance with the structure **7a**.

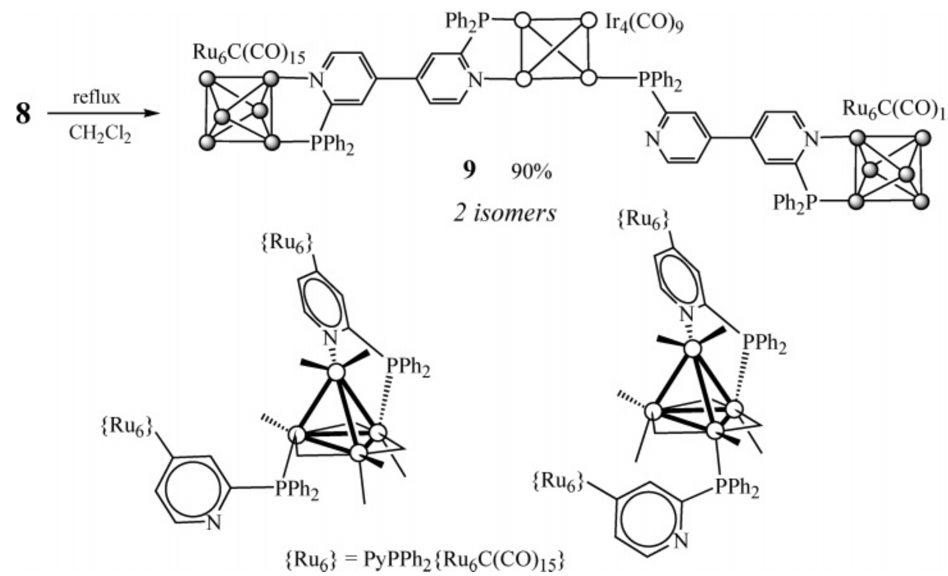
The cluster **7** reacts further with **4** to give the triple-cluster complex $[(Ru_6C(CO)_{15}\{\mu,\kappa^2{:}\kappa^1\text{-dpbp}\})_2Ir_4(CO)_{10}]$ (**8**) in 75% yield (Scheme 3). The compound **8** can be also obtained by a direct reaction of 2.2 equiv of **4** with $[Ir_4(CO)_{11}Br][NBu_4]$.

The mass spectrum of **8** exhibits a molecular ion at *m/z* 4176. The NMR spectroscopic data obtained for **8** make it possible to suggest the structure of this cluster, shown in Scheme 3. Two $\{Ru_6C(CO)_{15}dpbp\}$ fragments are coordinated in a κ^1 (through phosphorus) mode to the basal iridium atoms in axial and equatorial positions. The same coordination mode of two pyridylphosphine ligands was observed earlier in the $[Ir_4(CO)_{10}(\kappa^1\text{-}PPh_2Py)_2]$ cluster.[64] In accordance with this structure, the $^{31}P\{^1H\}$ spectrum of **8** at room temperature shows three signals—a low-field (28.1 ppm) asymmetric unresolved resonance of double intensity that obviously corresponds to the phosphorus atoms bound to the $\{Ru_6C\}$ moieties and two broader high-field signals (16.4 and −14.0 ppm), which can be assigned to the iridium-bonded phosphorus atoms. Broadening of the latter signals may be explained by the scrambling process in the carbonyl environment, which induces the exchange of axial and equatorial positions of the phosphorus ligands. Similar dynamic behavior was observed earlier in the $[Ir_4(CO)_{10}(PPh_2Py)_2]$ congener.[64]

The $\{Ir_4\}$ core of cluster **8** is unstable, undergoing spontaneous loss of a CO and P,N bridge closure to form $[Ru_6C(CO)_{15}\{\mu,\kappa^2{:}\kappa^1\text{-dpbp}\}Ir_4(CO)_9\{\mu,\kappa^2{:}\mu,\kappa^2\text{-dpbp}\}Ru_6C(CO)_{15}]$ (**9**) (Scheme 4). The reaction occurs slowly at room temperature, and gentle reflux of a dichloromethane solution of **8** under nitrogen is a convenient synthetic route to **9**. The mass spectrum of **9** is consistent with the composition suggested above and shows the signal of the molecular ion at *m/z* 4148. The room-temperature $^{31}P\{^1H\}$ NMR spectrum of **9** in $CDCl_3$ solution shows two groups of signals.

The low-field group in the 27.7−27.3 ppm region is associated with the phosphorus atoms connected to the $\{Ru_6C\}$ cores. The high-field-shifted signals are ascribed to the iridium-bound phosphorus nuclei. Two well-

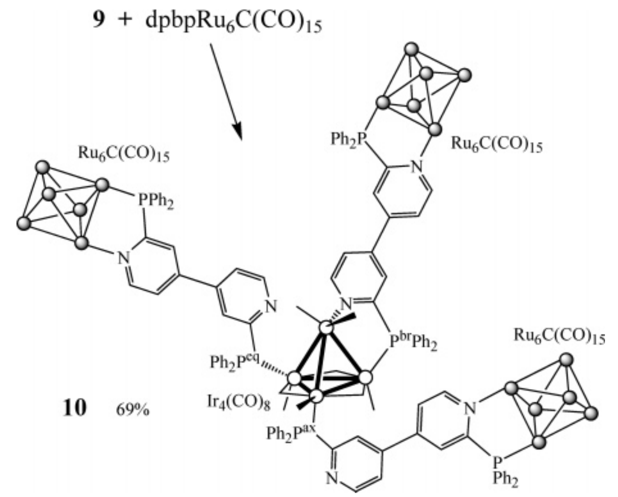
Scheme 4



separated singlets (−7.6 and −12.0 ppm) and a broad resonance (−14.5 ppm) point to the existence of two different isomers of **9** presented in solution in an approximately 2/3 ratio. The shape of the line at −14.5 ppm indicates that a scrambling process occurs in the molecule at 293 K. At lower temperature (253 K) the scrambling process is frozen, which results in the appearance of four narrow signals between −7.8 and −14.8 ppm, while the isomer ratio remains virtually the same (Figure S2, ^{31}P VT). The high-field shift of these resonances and comparison with the spectra of **8**, $[Ir_4(CO)_{10}(PPh_2Py)_2]$,[64] and $[Ir_4(CO)_8(\mu\text{-}PPh_2Py)(PPh_2Py)_2]$[29] indicate that in both isomers of **9** the phosphorus atom of the κ^1-coordinated $\{dpbpRu_6C(CO)_{15}\}$ "ligand" occupies an axial position at the basal iridium center. The chemical shift of the phosphorus atom disposed at an equatorial position of the $\{Ir_4\}$ cluster was found to appear in a low-field region between 10.44[64] and 28.3[29] ppm. Asymmetric coordination of the bridging $\{dpbpRu_6C(CO)_{15}\}$ group at the $\{Ir_4\}$ core (Scheme 4) dictates the difference between two axial positions at which the other terminal $\{dpbpRu_6C(CO)_{15}\}$ "ligand" can be coordinated and therefore explains the isomerization observed. A similar asymmetry was observed earlier in the $[Ir_4(CO)_8(\mu\text{-}PPh_2Py)(PPh_2Py)_2]$[29] congener of **9**. We theorize that in **9** the bridging coordination occurs analogously, which gives rise to the appearance of two isomers. The cluster **9** exhibits hemilability of the pyridyl ring coordinated at the iridium metal core. Saturation of the dichloromethane solution containing **9** with CO results in regeneration of **8**. Similar behavior was observed for the complexes $[Ir_4(CO)_{10}(PPh_2Py)_2(\mu\text{-}PPh_2Py)]$[29] and $[Ir_2Rh_2(CO)_{10}(\eta^4\text{-}COD)]$.[69]

The hemilability of **9** and reversible recoordination of CO to this cluster indicate that other two-electron donors can be added to this cluster under similar conditions. The reaction between **9** and **4** (molar ratio ca. 1/1.4) in dichloromethane solution results in complete consumption of the starting cluster **9** to form an unidentified intermediate that proved to be unstable on silica, which did not allow its separation and characterization. However, gentle reflux of the reaction mixture for 10 h leads to formation of the cluster $[(Ru_6C(CO)_{15}\{\mu,\kappa^2{:}\kappa^1\text{-}dpbp\})_2Ir_4(CO)_8(\{\mu,\kappa^2{:}\mu,\kappa^2\text{-}dpbp\}Ru_6C(CO)_{15})]$ (**10**) in good yield (69%) (Scheme 5).

Scheme 5



It is very likely that the noncoordinated phosphorus atom of the $\{\mu,\kappa^2\text{-}dpbpRu_6C(CO)_{15}\}$ "ligand" initially substitutes the coordinated pyridyl functionality in **9** to give the unstable intermediate $[(Ru_6C(CO)_{15}\{\mu,\kappa^2{:}\kappa^1\text{-}dpbp\})_3Ir_4(CO)_9]$, where all three $\{dpbpRu_6C(CO)_{15}\}$ fragments are bonded to the $\{Ir_4\}$ core through the phosphorus atoms only. Further heating of the reaction mixture results in the loss of a CO ligand and coordination of one of the pyridyl functions to an iridium atom to afford the final product **10**. The ESI mass spectrum of **10** gave a signal for the molecular ion at *m/z* 5682 (calculated 5684). The isotopic distribution pattern was not resolved in this broadened peak, but it is clearly visible in the signal corresponding to M^{2+} at $m/2z$ 2842 and fits perfectly with the calculated isotopic peak. The $^{31}P\{^1H\}$ NMR spectrum of **10** in CD_2Cl_2 confirms the proposed structure and exhibits six well-separated signals of equal relative intensities. Three closely located singlets (28.3, 28.1, and 27.9 ppm) correspond to phosphorus atoms coordinated at the $\{Ru_6C\}$ cores. Three other multiplets are associated with the iridium-coordinated phosphorus atoms (29.9 ppm, dd (^3J(P−P) = 47.9 Hz and ca. 2 Hz, poorly resolved), −8.7 ppm, dd, (^3J(P−P) = 47.9 and 2.7 Hz), and −11.9 t ($^3J_{av}$(P−P) = 2.4 Hz)) and resemble closely the signals observed in the $^{31}P\{^1H\}$ NMR spectrum of the $[Ir_4(CO)_{10}(PPh_2Py)_2(\mu\text{-}PPh_2Py)]$ cluster: 28.3 ppm (P_{eq}; $^3J(P_{eq}-P_{br})$ = 48.2 Hz, $^3J(P_{eq}-P_{ax})$ = 2.4 Hz), −12.2 (P_{br}; $^3J(P_{br}-P_{eq})$ = 48.2 Hz, $^3J(P_{br}-P_{ax})$ = 2.4 Hz), −13.4 (P_{ax}; $^3J(P_{ax}-P_{br})$ = 2.4 Hz, $^3J(P_{ax}-P_{eq})$ = 2.4 Hz).[29] This similarity allows assignment of two multiplets (29.9 and −8.7 ppm) in the spectrum of **10** to the equatorial κ^1 and bridging μ,κ^2 coordinated ligands, whereas the triplet at −11.9 ppm corresponds to the axial κ^1 pyridylphosphine. This triplet structure obviously masks a poorly resolved dd resonance with similar values of coupling constants. The ^{1}H NMR spectrum of **10** (Figure S3) is also in agreement with the proposed structure and demonstrates the presence of three nonequivalent $\{\mu,\kappa^2\text{-}dpbpRu_6C(CO)_{15}\}$ "ligands" in the molecule. It displays a well-separated low-field signal of the H^6 pyridyl protons (nonresolved combination of three doublets centered at 9.24 ppm, 3H), which is associated with the ruthenium-coordinated pyridyl moieties. This value of the chemical shift is very similar to those found for **3** (9.34 ppm) and **5** (9.31 ppm). In turn, three doublets of the H^6 atoms found at 8.79 ppm (J(H−H) = 4.8 Hz), 8.64 ppm (J(H−H) = 5.2 Hz), and 8.56 ppm (J(H−H) = 5.6 Hz) are evidently displayed by the noncoordinated and $\{Ir_4\}$-bound pyridyl rings.

In summary, we have presented the synthesis and characterization of the novel heteropolydentate (P,N−P,N) ligand designed to serve as a linking unit between different metal centers. Interaction of this ligand with the hexanuclear ruthenium and rhodium and tetranuclear iridium clusters led to formation of three double complexes where two cluster fragments are linked together. The availability of the $\{Ru_6C(CO)_{15}dpbp\}$ complex bearing accessible P and N donor atoms allowed for the synthesis of a few heterocluster compounds and the mixed-valence complex $[(Ru_6C(CO)_{15}dpbp)_2Rh_2(CO)Cl_2]$. The substitution of several CO groups in the parent $[Ir_4(CO)_{12}]$ cluster gave an opportunity to dispose more

---

(69) Bondietti, G.; Suardi, G.; Ros, R.; Roulet, R.; Grepioni, F.; Braga, D. *Helv. Chim. Acta* **1993**, *76*, 2913.

than one $\{Ru_6C(CO)_{15}dpbp\}$ "ligand" on the tetrairidium core. Thus, the tri- and tetracluster supermolecules were obtained using a simple and convenient route. The identity and stereochemistry of these complexes have been established on the basis of ^1H and ^{31}P NMR and ESI^+ mass spectroscopic evidence along with the comparative analysis of the spectroscopic data for analogous pyridylphosphine complexes.[29,64] The synthetic approach used in this study illustrates a possibility of efficient preparation of nanosized molecules based on metal clusters and polydentate ligands. A detailed investigation of the properties of these complexes and the synthesis of more sophisticated molecules are underway.

Acknowledgment. This research has been supported by the grants from the Academy of Finland (I.O.K., M.H., T.A.P.). We gratefully acknowledge Prof. R. T. Kelly (Boston College) for his valuable advice in preparation of 2,2′-dibromodipyridine and Dr. S. I. Selivanov (St. Petersburg State University) for 2D NMR measurements.

Supporting Information Available: Tables and figures giving crystallographic data and ^1H COSY, ^{31}P VT, and ^1H NMR spectra; crystallographic data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0502032