Organometallics **1993,** *12,* 4211–4214 4211

Heterobimetallic Indenyl Complexes. Synthesis and Structure of *cis*-$[Cr(CO)_3(indenyl)]RhL_2$ (L_2 = Norbornadiene, $(CO)_2$)

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Received May 5, 1993®

Summary: Reaction of the potassium salt of [(η^6-*indenyl*)$Cr(CO)_3$] *at* −30 °C *in THF with* $[Rh(Cl)NBD]_2$ (*NBD* = *norbornadiene*) *yields cis*-[$Cr(CO)_3$(*indenyl*)]*Rh*(*NBD*), **2**. *Bubbling CO through a* CH_2Cl_2 *solution of* **2** *produces cis*-[$Cr(CO)_3$(*indenyl*)]$Rh(CO)_2$, **3** *in quantitative yield. X-ray analyses show for indenyl–Rh*(*NBD*), **1**: a = 17.506(8) Å, b 11.427(6) Å, c = 5.979(4) Å, β = 90.8(2)°, *space group* $P2_1/n$. *For* **2**: a = 11.098(6) Å, b 17.684(8) Å, c = 8.253(5) Å, β = 99.7(2)°, *space group* $P2_1/a$. *For* **3**: a = 16.558(8) Å, b 12.483(8) Å, c = 6.629(4) Å, *space group* $P2_12_12_1$. *Both* **2** *and* **3** *have a doubly-bent indenyl moiety and show strongly distorted coordination modes toward the indenyl ligand of both metals. The driving force leading to such highly distorted structures probably arises mainly from a metal–metal interaction.*

Introduction

It is widely documented that d^8-[(η-indenyl)RhL_2] complexes show a small but significant slip distortion from the η^5 toward the η^3 coordination mode in the ground state.[1] The same complexes display an enhanced reactivity in ligand substitution reactions as well as in catalyzed cyclotrimerization of alkynes[2] compared with their cyclopentadienyl analogues. This behavior has been attributed to a facile $\eta^5 \rightarrow \eta^3$ ring slippage phenomenon which is favored in the case of indenyl compounds because of rearomatization of the benzene ring in the transition state ("indenyl effect").[3]

In a previous communication[4] we reported the synthesis and X-ray structure of the heterobimetallic complex [$Cr(CO)_3$(indenyl)]Rh(COD), in which the two inorganic units are *anti* with respect to the indenyl plane. Even though the structural parameters of the Rh–cyclopentadienyl ring subunit of this bimetallic complex are very similar to those found for the monometallic indenyl–Rh(COD),[5] the two complexes have been shown to behave quite differently both as catalysts and in ligand substitution reactions, the bimetallic one being far more reactive.[6]

Complexes with two metal centers which are connected by a bridging organic ligand are known. Examples for an *antifacial* variant are provided by the heterobimetallic indenyl complexes previously reported[4,6–8] and by the *pseudo*-triple-decker complexes in which the metallic units CpM (M = Rh, Co) can coordinate to a tube-shaped tetraolefin, *viz.*, cyclooctatetraene (COT),[9a] or to a condensed polyaromatic skeleton, *viz.*, naphthalene.[9b,c] Conversely, examples of a *synfacial* arrangement to a bridging organic ligand are relatively less numerous; the ligand (COT,[9a,10] cycloheptatrienyl,[11] or even benzene itself[12]) in this case can coordinate to the metals in different ways by assuming different conformations. The bridging ring therefore adopts different hapticities according to the electron count which gives both metal atoms a closed shell if a bond between the two nuclei is taken into account. When the bridging ligand is a rigid arene, in contrast with the highly flexible COT, more severe molecular constraints are required to allow the formation of a *cis* complex, including the bending of the arene frame.

During the preparation of *trans*-[$Cr(CO)_3$(indenyl)]Rh(COD), we did not observe the presence of a *cis* isomer

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® Abstract published in *Advance ACS Abstracts*, September 1, 1993.

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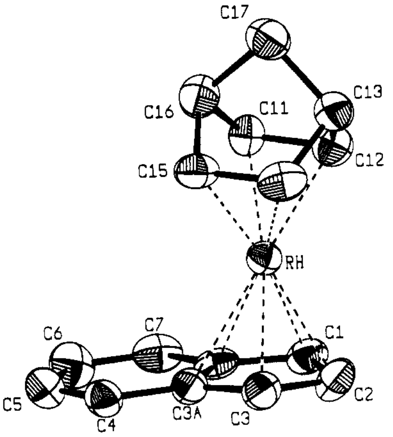

Figure 1. ORTEP view of 1. Selected bond lengths (Å): Rh–C_1 2.224(5), Rh–C_2 2.240(5), Rh–C_3 2.228(5), Rh–C_{3a} 2.401(3), Rh–C_{7a} 2.388(4), C_{3a}–C_{7a} 1.42(1).

among the reaction products. However, we succeeded in obtaining the *cis* isomer as the only product if norbornadiene (NBD) instead of COD is used as an ancillary ligand at rhodium. The synthesis and X-ray structures of the two new heterobimetallic complexes, [Cr(CO)$_3$(indenyl)]RhL$_2$ (**2**, L$_2$ = norbornadiene; **3**, L = CO), in which two 12-electron organometallic moieties are *cis* with respect to the indenyl frame, are described herein. The X-ray structure of the monometallic indenyl-Rh(NBD) complex, **1** (NBD = norbornadiene), is also reported for comparison. To our knowledge, **2** and **3** are the first examples of *cis* heterobimetallic complexes of the indenyl ligand, the only related species being the homobimetallic complex *cis*-diindenyldivanadium.[13]

Results and Discussion

The reaction of the η^6-indenyl–Cr(CO)$_3$ anion at −30 °C in THF with [Rh(Cl)(COD)]$_2$ yielded *trans*-[Cr(CO)$_3$(indenyl)]Rh(COD).[4] In contrast, when the same anion was reacted with [Rh(Cl)(NBD)]$_2$ under the same conditions, a solid residue was isolated and crystallized from CH_2Cl_2–hexane to give brown crystals of a product which was identified (*vide infra*) as *cis*-[Cr(CO)$_3$(indenyl)]Rh(NBD), **2**. Bubbling CO through a CH_2Cl_2 solution of **2** produced *cis*-[Cr(CO)$_3$(indenyl)]Rh(CO)$_2$, **3** in quantitative yield.

Figure 1 shows the molecular structure of complex **1** together with some relevant geometrical parameters. The distances from Rh to the carbon atoms of the indenyl ligand indicate a distorted η^5 coordination as found for several other (η-indenyl)RhL$_2$ complexes.[1] This distortion arises from a sensible puckering of the [C_1, C_2, C_3] plane with respect to the remainder of the indenyl group, the corresponding hinge angle being *ca.* 10°. The Rh–C_{3a} and Rh–C_{7a} distances are 2.401(3) and 2.388(4) Å, respectively; all the Rh–C_1, Rh–C_2, and Rh–C_3 distances are *ca.* 2.23(1) Å, which indicates the absence of any shift of the metal toward the outermost C_2 carbon atom. The planes defined by [C_1, C_2, C_3] of the indenyl frame and by [C_{11}, C_{12}, C_{14}, C_{15}] of NBD are almost exactly parallel to each other, showing an undistorted coordination about the rhodium atom.

The molecular structure of **2** is shown in Figure 2. The distances from rhodium to the ring junction atoms C_{3a} (2.567(3) Å) and C_{7a} (2.552(3) Å) are *ca.* 0.31 Å longer than Rh–C_1 (2.234(4) Å), Rh–C_3 (2.254(3) Å). The plane defined by [C_1, C_2, C_3] forms a hinge angle of *ca.* 12° with the planar moiety [C_3, C_{3a}, C_4, C_7, C_{7a}, C_1]; moreover, a relevant shift of Rh toward C_2 (0.08–0.09 Å) is observed. The distances from chromium to the atoms C_{3a} (2.448(3) Å) and C_{7a} (2.448(3) Å) are *ca.* 0.19 Å longer than Cr–C_4 (2.258(3) Å) and Cr–C_7 (2.271(3) Å) and *ca.* 0.25 Å longer than Cr–C_5 (2.208(4) Å) and C–C_6 (2.197(5) Å); the plane defined by [C_4, C_5, C_6, C_7] forms a hinge angle of *ca.* 11° with the planar frame [C_3, C_{3a}, C_4, C_7, C_{7a}, C_1]. A shift of Cr toward the outermost carbon atoms of the benzene group C_5 and C_6 (*ca.* 0.04–0.05 Å) is observed. The junction bond C_{3a}–C_{7a} is elongated up to 1.456(4) Å and seems to participate to a less extent in the resonance of the indenyl system. Probably, the two π-electrons are partially engaged to give rise to a multicenter bond in which rhodium and chromium are also involved. Thus, the Cr and Rh coordination modes are both highly distorted from ideal η^6 and η^5 hapticities.

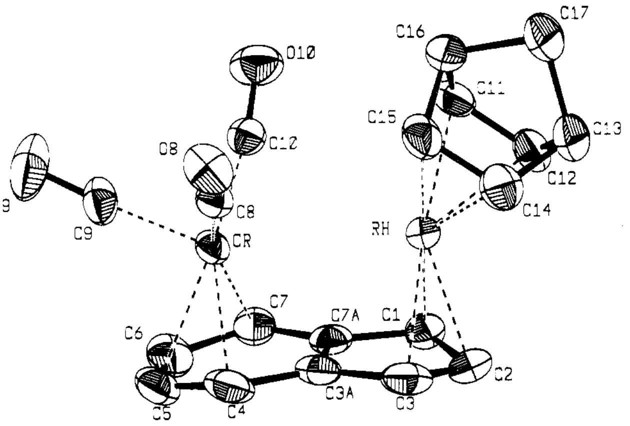

Figure 2. ORTEP view of 2. Selected bond lengths (Å): Rh–C_1 2.234(4), Rh–C_2 2.164(4), Rh–C_3 2.254(3), Rh–C_{3a} 2.567(3), Rh–C_{7a} 2.552(3), Cr–C_{3a} 2.448(3), Cr–C_{7a} 2.448(3), Cr–C_4 2.258(3) Cr–C_5 2.208(4), Cr–C_6 2.197(5), Cr–C_7 2.271(3), C_{3a}–C_{7a} 1.457(3), C_1–C_{7a} 1.440(4), C_3–C_{3a} 1.434(5), Rh···Cr 3.181(1). Bond angles (deg): C_9–Cr–C_{10} 83.0(2), C_9–Cr–C_8 87.1(2), C_8–Cr–C_{10} 90.5(2), Cr–C_{10}–O_{10} 171.9(3), Cr–C_9–O_9 176.8(4), Cr–C_8–O_8 175.3(3).

This conclusion is corroborated by the NMR results which indicate that the same structural features also persist in solution. The minor coordinative engagement of C_{3a} and C_{7a} in **2** with respect to **1** is suggested by the effect of complexation with Cr(CO)$_3$ on their chemical shift value ($\Delta\delta$ = −4.33 ppm); this value is substantially lower than that found in a wide series of *trans*-(*Cr,Rh*)-indenyl complexes (mean $\Delta\delta$ = −26.6 ppm)[7] and, in general, for the quaternary carbon atoms in arenes.[14] Moreover, the tetrahedralization of the C_4 and C_7 carbon atoms is evidenced by the much more pronounced upfield shift of the resonances of the nuclei in these pivot positions with respect to those of the nuclei in positions 5 and 6, as shown by comparing the NMR data of **1** and **2** [$\Delta\delta(C_4,C_7)$ = −43.84 ppm, $\Delta\delta(C_5,C_6)$ = −33.62 ppm; $\Delta\delta(H_4,H_7)$ = −2.77 ppm, $\Delta\delta(H_5,H_6)$ = −1.83 ppm]. The increasing of the hinge angle from 10 to 12° on going from **1** to **2** is also in accord with the negative $\Delta\delta(C_1,C_3)$ value (−13.22 ppm). Finally, the increased importance in **2** of an η^3 bonding mode of rhodium toward the five-membered ring (and then of the

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allenyl character of the [C_1–C_5] subunit) is suggested by the positive value $\Delta\delta(H_2) = +1.05$ ppm and, in general, by the higher chemical shift differences found for both by ^1H and ^{13}C nuclei in positions 1 and 3 with respect to those in position 2 upon complexation with $Cr(CO)_3$, as previously discussed.[4,7]

Besides the above mentioned features, the structure of **2** exhibits the following molecular constraints: (i) distortion of the coordination about Rh, as evidenced by the large dihedral angle (*ca.* 23°) between the planes defined by [C_1, C_2, C_3] of the indenyl frame and [C_{11}, C_{12}, C_{14}, C_{15}] of NBD in comparison with their parallelism in the case of complex **1**; (ii) tightening of the bond angles C_{10}–Cr–C_9 and C_8–Cr–C_9 to 83.0(2) and 87.1(2)°, respectively (bond angles Cr–C_{10}–O_{10} and Cr–C_8–O_8 deviated from the normal values of *ca.* 9 and 5°, respectively); (iii) short nonbonded distances between the CO groups and the NBD ligand, *i.e.*, $C_{11}\cdots O_{10}$ 3.13 Å, $C_{11}\cdots C_{10}$ 3.19 Å, $C_{15}\cdots C_8$ 3.27 Å, $C_{15}\cdots O_8$ 3.30 Å.

The driving force leading to such large distortions, and in particular to the doubly-bent indenyl ligand, seems to be the bond interaction Rh–Cr at a distance of 3.181(1) Å involving also the two π-electrons of C_{3a} and C_{7a}. As the two metals move apart from their ideal η^6,η^5 coordination, it is possible that their incipient coordinative unsaturation would result in the onset of Cr–Rh interaction. Moreover, the NBD hydrogen atoms H_{15} and H_{11}, located at distances of 2.68 and 2.55 Å from the midpoint of the bonds C_8–O_8 and C_{10}–O_{10}, respectively, cannot be supposed to undergo strongly repulsive van der Waals interactions; on the contrary, we believe that important stabilizing interactions are involved here, as found recently in several similar complexes, but never at such short distances.[14]

These facts raise the question of whether the conformational parameters exhibited by **2** are controlled by the nature and the steric encumbrance of the ancillary ligands bonded to rhodium. The crystal structure of *trans*-[Cr(CO)$_3$(indenyl)]Rh(COD) and the results in the synthesis[4] suggest that the bulkier COD ligand makes more difficult the formation of the *cis* isomer. As a matter of fact, suitable models indicate that an overcrowded number of hydrogen atoms of the COD moiety would produce repulsive interactions with the $Cr(CO)_3$ group in a *cis* configuration. Thus, we prepared and studied the crystal structure of complex **3** having less bulky ligands on rhodium, with the expectation of a stronger Rh⋯Cr bond as a consequence of weaker stereochemical hindrances in a *cis* configuration.

The molecular structure of **3** is shown in Figure 3. The distances of Rh and Cr from the indenyl carbon atoms indicate highly distorted η^5 and η^6 hapticities, respectively. The plane defined by [C_1, C_2, C_3] forms a hinge angle of *ca.* 15° with the plane [C_3, C_{3a}, C_4, C_7, C_{7a}, C_1]; the hinge angle between the planes [C_4, C_5, C_6, C_7] and [C_3, C_{3a}, C_4, C_7, C_{7a}, C_1] is lowered to *ca.* 7°. These distortions are of the same magnitude with respect to the monometallic complex indenyl-Rh(CO)$_2$[15] as those found on going from **1** to **2**. The geometrical parameters of the $Cr(CO)_3$ group are nearly the same as in **2**. The bond length C_{3a}–C_{7a} is 1.430(5) Å, while the bond lengths C_1–C_{7a} and C_3–C_{3a} are both 1.465(6) Å. These values are in agreement with a stronger allylic character of the [C_1, C_2, C_3] frame and a less distorted η^6 coordination mode of Cr. The carbonyl groups bonded to Rh and to Cr are disposed in front of each other with distances $C_8\cdots C_{11}$, $C_{10}\cdots C_{12}$, $C_{12}\cdots O_{10}$, and $C_{11}\cdots O_8$ of *ca.* 3.14 Å. Nevertheless, these values correspond to less repulsive interactions than those found in **2** owing to the different nature and orientation of the groups involved. As a whole the molecular constraints in **3** seem to be more released, allowing a decrease of the Rh⋯Cr distance to 3.077(1) Å, so confirming its bonding nature.

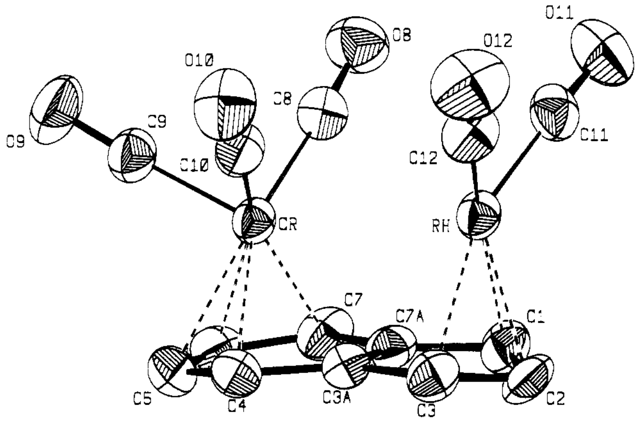

Figure 3. ORTEP view of **3**. Selected bond lengths (Å): Rh–C_1 2.198(4), Rh–C_2 2.189(4), Rh–C_3 2.248(5), Rh–C_{3a} 2.576(4), Rh–C_{7a} 2.542(4), Cr–C_{3a} 2.375(4), Cr–C_{7a} 2.401(4), Cr–C_4 2.239(4) Cr–C_5 2.181(5), Cr–C_6 2.188(4), Cr–C_7 2.257(4), C_{3a}–C_{7a} 1.430(5), C_1–C_{7a} 1.465(6), C_3–C_{3a} 1.465(6), Rh⋯Cr 3.077(1). Bond angles (deg): C_9–Cr–C_{10} 85.1(2), C_9–Cr–C_8 85.7(2), C_8–Cr–C_{10} 95.5(2), Cr–C_{10}–O_{10} 175.3(3), Cr–C_9–O_9 178.0(5), Cr–C_8–O_8 174.5(4), Rh–C_{11}–O_{11} 176.8(4), Rh–C_{12}–O_{12} 177.2(4).

Experimental Section

General Comments. All reactions were carried out under oxygen-free argon. Solvents were purified according to standard procedures,[16] distilled, and purged with argon before use. Commercial grade cycloocta-1,5-diene and norbornadiene (Aldrich) were dried over $MgSO_4$ and distilled just before use. The Rhodium complexes were crystallized from methylene chloride–pentane and gave elemental analyses within ±0.2% of the calculated values. Instruments: mass spectrum, 70 eV-EI, VG-16 MicroMass; IR, Perkin-Elmer 1600 FT-IR; NMR, Bruker AM-400 (^1H, 400.133 MHz; ^{13}C, 100.614 MHz). The ^1H and ^{13}C spectra were recorded in CD_2Cl_2 solution at 298 K and are in units of ppm referenced to internal Me_4Si. IR spectra were run as CH_2Cl_2 solutions within CaF_2 windows. Melting points are uncorrected. $Cr(CO)_3$–indene was obtained from indene and $(NH_3)_3Cr(CO)_3$[17] and it was metalated with oil-free KH (Aldrich) in THF at −30 °C.[18]

Preparation of 1. Complex **1** was prepared according to Salzer.[19] Mp = 137–139 °C. ^1H NMR (assignments confirmed by {^1H}–^1H NOE): δ = 7.28 and 7.02 (m, 2H each, AA′BB′, $H_{4,7}$ and $H_{5,6}$, respectively), 6.02 (m, 1H, $J(^{103}Rh\text{–}H) \cong 2.0$ Hz, H_2), 5.14 (m, 2H, $H_{1,3}$): (NBD resonances) δ = 3.31 (m, 4H, olefin protons), 3.13 (m, 2H, bridgehead protons), 0.86 (m, 2H, CH_2). {^1H}–^{13}C NMR (100.61 MHz, CD_2Cl_2, 25 °C, assignments made by selective ^1H-decoupling): δ = 122.12 ($C_{5,6}$), 119.78 ($C_{4,7}$), 110.75 (d, $J(^{103}Rh\text{–}C) < 0.4$ Hz, $C_{3a,7a}$), 91.52 (d, $J(^{103}Rh\text{–}C) = 5.4$ Hz, C_2), 74.01 (d, $J(^{103}Rh\text{–}C) = 4.5$ Hz, $C_{1,3}$); (NBD resonances) δ =

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58.5 (d, $J(^{103}\mathrm{Rh{-}C}) = 6.3$ Hz, CH_2), 47.5 (d, $J(^{103}\mathrm{Rh{-}C}) = 5.3$ Hz, bridgehead carbons), 38.0 (d, $J(^{103}\mathrm{Rh{-}C}) = 13.8$ Hz, olefin carbons).

Preparation of 2. A saturated solution of $[Rh(Cl)(NBD)]_2$ in THF at −30 °C was treated with an equivalent amount of $Cr(CO)_3$–indenylpotassium in THF maintained at −30 °C. The brownish mixture was slowly warmed to room temperature, filtered, and evaporated to dryness and the residue crystallized (red-brown crystals). Yield = 70%. Mp = 180–183 °C. MS: *m/z* 446 (M^+). IR: 1943 (vs), 1867 (vs) cm^{-1} ($C{\equiv}O$). ^{1}H NMR: $\delta = 7.05$ (m, 1H, $J(^{103}\mathrm{Rh{-}H}) \cong 2.0$ Hz, H_2), 4.05 (m, 2H, $H_{1,3}$), 5.19 and 4.51 (m, 2H each, AA′BB′, $H_{5,6}$ and $H_{4,7}$, respectively); (NBD resonances) $\delta = 3.77$ (m, 4H, olefin protons), 3.62 (m, 2H, bridgehead protons), 1.10 (m, 2H, CH_2). $\{^1H\}$–^{13}C NMR: $\delta = 236.06$ ($C{\equiv}O$), 88.50 ($C_{5,6}$), 75.94 ($C_{4,7}$), 106.42 (d, $J(^{103}\mathrm{Rh{-}C}) = 0.8$ Hz, $C_{3a,7a}$), 88.46 (d, $J(^{103}\mathrm{Rh{-}C}) = 6.3$ Hz, C_2), 60.79 (d, $J(^{103}\mathrm{Rh{-}C}) = 5.3$ Hz, $C_{1,3}$); (NBD resonances) $\delta = 45.15$ (d, $J(^{103}\mathrm{Rh{-}C}) = 9.4$ Hz, olefin carbons), 48.00 (d, $J(^{103}\mathrm{Rh{-}C}) = 2.5$ Hz, bridgehead carbons), 59.52 (d, $J(^{103}\mathrm{Rh{-}C}) = 7.2$ Hz, CH_2).

Preparation of 3. A stream of CO was bubbled through a CH_2Cl_2 solution of **2** at room temperature to obtain a quantitative yield of the product (red-brown crystals). Mp = 196 °C dec. MS: *m/z* 410 (M^+). IR 2056 (s), 2000 (s), 1951 (vs), 1885 (vs) cm^{-1} ($C{\equiv}O$). ^{1}H NMR: $\delta = 6.45$ (m, 1H, $J(^{103}\mathrm{Rh{-}H}) \cong 2.0$ Hz, H_2), 4.55 (m, 2H, $H_{1,3}$), 5.35 and 4.62 (m, 2H each, AA′BB′, $H_{5,6}$ and $H_{4,7}$, respectively). $\{^1H\}$–^{13}C NMR: $\delta = 234.83$ ($Cr{-}C{\equiv}O$), 190.62 (d, $J(^{103}\mathrm{Rh{-}C}) = 82.0$ Hz, $Rh{-}C{\equiv}O$), 90.53 ($C_{5,6}$), 75.39 ($C_{4,7}$), 109.70 (d, $J(^{103}\mathrm{Rh{-}C}) \leq 0.4$ Hz, $C_{3a,7a}$), 89.47 (d, $J(^{103}\mathrm{Rh{-}C}) = 7.4$ Hz, C_2), 61.11 (d, $J(^{103}\mathrm{Rh{-}C}) = 3.8$ Hz, $C_{1,3}$).

Crystallography. Crystal structure analyses: Philips PW-100 computer controlled four circle diffractometer, Mo Kα radiation, graphite monochromator, 298 K, empirical absorption corrections, SHELX-76 program,[20] Patterson methods, least-squares fit. Complex **1**: monoclinic, space group $P2_1/n$, $a = 17.506(8)$ Å, $b = 11.427(6)$ Å, $c = 5.979(4)$ Å, $\beta = 90.8(1)°$, $V = 1195.93$ Å^3, $Z = 4$, $\rho = 1.72$ g cm^{-3}, $\mu = 12.62$ cm^{-1}, crystal dimensions 0.25 × 0.30 × 0.20 mm, θ–2θ scan method, $2\theta_{max}$ 45°, 1617 unique reflections ($F_o^2 > 2\sigma(F_o^2)$), R (on F_0) = 0.072. Complex **2**: monoclinic space group $P2_1/a$, $a = 11.098(6)$ Å, $b = 17.684(8)$ Å, $c = 8.253(5)$ Å, $\beta = 99.7(2)°$, $V = 1596.55$ Å^3, $Z = 4$, $\rho = 1.86$ g cm^{-3}, $\mu = 18.19$ cm^{-1}, crystal dimensions 0.35 × 0.35 × 0.20 mm, θ–2θ scan method, $2\theta_{max}$ 45°, 3128 unique reflections ($F_o^2 \geq 2\sigma(F_o^2)$), R (on F_0) = 0.032. Complex **3**: orthorhombic, space group $P2_12_12_1$, $a = 16.558(8)$ Å, $b = 12.483(6)$ Å, $c = 6.629(4)$ Å, $V = 1370.17$ Å^3, $Z = 4$, $\rho = 1.99$ g cm^{-3}, $\mu = 21.25$ cm^{-1}, crystal dimensions 0.35 × 0.35 × 0.30 mm, θ–2θ scan method, $2\theta_{max}$ 45°, 1845 unique reflections ($F_o^2 \geq 2\sigma(F_o^2)$), R (on F_o) = 0.028. In all cases the non-hydrogen atoms were refined with anisotropic temperature factors; the hydrogen atoms were calculated at idealized positions ($U(H) = 0.10$ Å^2).

Acknowledgment. This work was supported in part by CNR through its Centro di Studio sugli Stati Molecolari, Radicalici ed Eccitati, Padova, Italy, and through its Progetto Finalizzato Chimica Fine II.

Supplementary Material Available: A summary of crystal and intensity data collection and full lists of bond distances and bond angles, fractional coordinates, anisotropic thermal parameters, and fractional coordinates of the H atoms for complexes **1**–**3** (8 pages). Ordering information is given on any current masthead page.

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