

Notes

A Stable Iridabenzene Formed from an Iridacyclopentadiene Where the Additional Ring-Carbon Atom Is Derived from a Thiocarbonyl Ligand

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Summary: The cationic thiocarbonyl complex $[\text{Ir}(\text{CS})(\text{MeCN})(\text{PPh}_3)_2][\text{CF}_3\text{SO}_3]$ (**1**) reacts sequentially with ethyne and LiCl to give the iridacyclopentadiene $\text{Ir}[\text{C}_4\text{H}_4]\text{Cl}(\text{CS})(\text{PPh}_3)_2$ (**2**), which in turn when heated with methyl triflate followed by addition of LiCl produces the stable, purple, iridabenzene $\text{Ir}[\text{C}_5\text{H}_4(\text{SMe}-1)]\text{Cl}_2(\text{PPh}_3)_2$ (**3**). This iridabenzene undergoes electrophilic aromatic bromination in the position *para* to the *Sme* substituent to form $\text{Ir}[\text{C}_5\text{H}_3(\text{SMe}-1)(\text{Br}-4)]\text{Br}_2(\text{PPh}_3)_2$ (**4**).

Introduction

Iridabenzenes are now well-established as a distinct class of compounds,¹ having been synthesized by four main approaches, involving (a) deprotonation of an iridacyclohexadiene (formed from initial introduction of a pentadienide ligand followed by ring closure from a C–H activation),² (b) rearrangement of a cyclopropenylvinyl ligand,³ (c) formal insertion of a either a vinylidene or carbene ligand into an iridacyclopentadiene followed by aromatization,⁴ and (d) oxidative ring contraction of an iridacycloheptatriene.⁵ These routes provide access to both five-coordinate and six-coordinate examples of iridabenzenes. Computational studies show that most metallabenzenes are unstable with respect to rearrangement to metal cyclopentadienyl complexes; however, of the model systems studied, six-coordinate iridium examples alone were more stable than the rearranged Cp complexes.⁶

The first metallabenzene was assembled from an osmium thiocarbonyl complex and ethyne,⁷ and since thiocarbonyl

complexes of iridium are well-known⁸ and the propensity of the thiocarbonyl ligand to participate in migratory insertion reactions is well-established,⁹ it is perhaps surprising that a similar approach has not been reported for iridabenzenes. Herein we describe that an iridacyclopentadiene incorporating a thiocarbonyl ligand can be induced, in the presence of methyl triflate, to insert the carbon atom of the CS ligand to form an iridabenzene bearing only one ring substituent. The lack of substituents allows examination of electrophilic substitution reactions, and it is demonstrated that this iridabenzene undergoes facile ring bromination in the position *para* to the *Sme* substituent.

Results and Discussion

Following the precedent established for the formation of the iridacyclopentadiene $[\text{Ir}[\text{C}_4\text{H}_4](\text{CO})(\text{MeCN})(\text{PPh}_3)_2]^{+10}$ from $[\text{Ir}(\text{CO})(\text{MeCN})(\text{PPh}_3)_2]^{+11}$ and ethyne, we treated the thiocarbonyl complex analogue $[\text{Ir}(\text{CS})(\text{MeCN})(\text{PPh}_3)_2][\text{CF}_3\text{SO}_3]$ (**1**) (derived from $\text{IrCl}(\text{CS})(\text{PPh}_3)_2$ ¹² and AgCF_3SO_3 ; characterizing data for **1** as well as for **2–4** are given in the Experimental Section) with ethyne, followed by LiCl , to form the neutral thiocarbonyl iridacyclopentadiene $\text{Ir}[\text{C}_4\text{H}_4]\text{Cl}(\text{CS})(\text{PPh}_3)_2$ (**2**) (see Scheme 1).

Complex **2** has been thoroughly characterized, including by a crystal structure determination (see below). In the ¹³C NMR spectrum of **2** the two iridium-bound carbon atoms of the iridacyclopentadiene ring appear as triplets (due to coupling with phosphorus) at 157.14 and 145.13 ppm, while in the ¹H NMR spectrum the protons attached to these carbon atoms are

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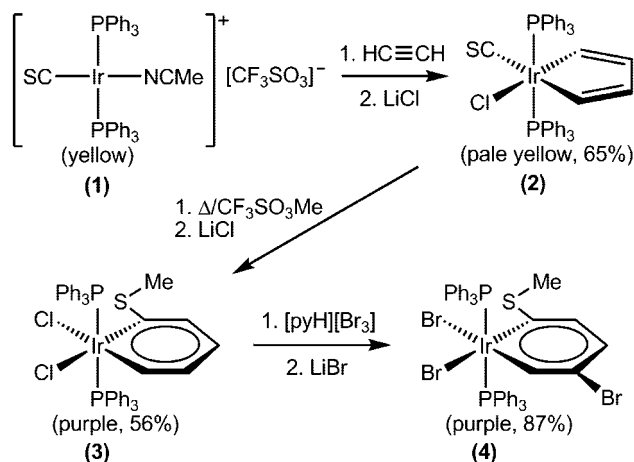
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Scheme 1. Synthesis of the Iridabenzene, 3, and Bromination of the Iridabenzene Ring to Give 4

observed as multiplets at 7.39 and 5.63 ppm. Complex **2** is a thermally stable compound and shows no evidence for insertion of the thiocarbonyl ligand into the iridacyclopentadiene ring on heating under reflux in benzene. However, when **2** is heated in the presence of methyl triflate, a color change is observed and addition of LiCl allows isolation of the purple, iridabenzene $\text{Ir}[\text{C}_5\text{H}_4(\text{SMe-1})]\text{Cl}_2(\text{PPh}_3)_2$ (**3**) in good yield (see Scheme 1). Possible explanations for the role of methyl triflate in promoting this reaction include either methylation at sulfur to form an intermediate cationic thiocarbonyl complex ($\text{Ir}(\text{C}_5\text{H}_4\text{SMe})(\text{CSMe})(\text{PPh}_3)_2$), which then undergoes insertion of the CSMe ligand to form **3** after addition of chloride, or chloride abstraction by methyl triflate, giving the cation $[\text{Ir}(\text{C}_5\text{H}_4)(\text{CS})(\text{PPh}_3)_2]^+$, which would be more prone to undergo a migratory insertion reaction before eventual methylation at sulfur and chloride addition to give **3**. The first possibility does not seem likely in view of the general observation that thiocarbonyl complexes with a $\nu(\text{CS})$ absorption above 1200 cm^{-1} do not undergo methylation at sulfur,¹³ and the second possibility seems no more likely since we have prepared the cation $[\text{Ir}(\text{C}_5\text{H}_4)(\text{MeCN})(\text{CS})(\text{PPh}_3)_2]^+$ and have been unable to induce CS insertion in this cation.¹⁴ A third possibility that cannot be excluded is that there is an equilibrium between compound **2** and the corresponding insertion product, which strongly favors **2**, but in the presence of methyl triflate this insertion product can be trapped by methylation, giving eventually **3**. In the absence of definitive evidence for the mechanism further speculation is unwarranted.

In common with other related metallabenzene,¹ complex **3** shows a characteristic low-field resonance for the iridium-bound CH at 12.31 ppm in the ^1H NMR spectrum, and the other ring protons have chemical shifts in the aromatic region. In the ^{13}C NMR spectrum, characteristic¹ low-field triplet resonances (229.12 and 198.19 ppm) are also observed for the metal-bound carbon atoms of the iridabenzene ring. It is interesting that although this synthesis involves a thermal reaction, there is no evidence for the rearrangement of the iridabenzene to an iridium cyclopentadienyl complex. This observation is consistent with computational results on model compounds, which suggest that iridabenzene with a six-coordinate iridium atom are resistant to this rearrangement.⁶

Complex **3** is obviously closely related to the blue osmabenzene $\text{Os}[\text{C}_5\text{H}_4(\text{SMe-1})]\text{I}(\text{CO})(\text{PPh}_3)_2$, where the metallabenzene ring is also assembled from two ethyne molecules and a CS

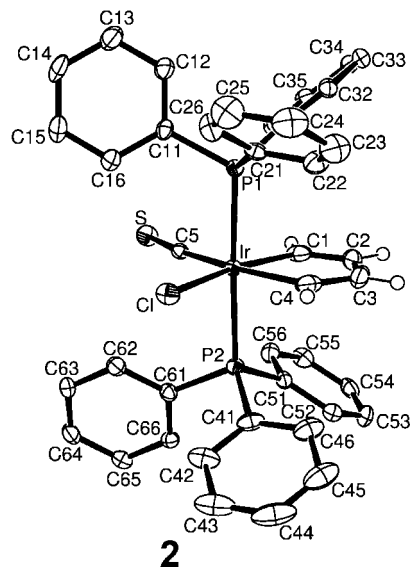


Figure 1. Molecular structure of **2** with thermal ellipsoids at the 50% probability level. Selected distances [Å]: Ir–C(5) 1.871(4), Ir–C(1) 2.051(3), Ir–C(4) 2.093(3), C(1)–C(2) 1.327(4), C(2)–C(3) 1.446(5), C(3)–C(4) 1.350(5), C(5)–S 1.555(4), Ir–Cl 2.4668(10).

ligand, ultimately methylated on sulfur.⁷ Theoretical studies suggest that the osmabenzene is assembled by a sequence of reactions that begins with combination of the thiocarbonyl with one ethyne to form a four-membered ring, which then undergoes ring-expansion with a second ethyne.^{6b} On the other hand the synthesis of the iridabenzene **3** involves a different order of assembly in that two ethyne molecules combine at iridium to first form an iridacyclopentadiene (complex **2**), which then incorporates the thiocarbonyl ligand in the presence of methyl triflate.

The crystal structure of complex **2** was determined and the molecular structure is shown in Figure 1 (crystal data for **2** as well as for **3** and **4** are given in the Supporting Information). Significant features are almost perfect planarity of the IrC_4 ring and bond distances appropriate for the localized bonding depicted in Scheme 1.

The crystal structure of complex **3** was determined and the molecular geometry is shown in Figure 2. The structural parameters are fully in accord with a metallabenzene formulation with equal Ir–C distances and with C–C ring distances reflecting delocalization.¹ There is distinct nonplanarity of the ring in that Ir is displaced 0.3072 Å from the least-squares plane through C(1), C(2), C(3), C(4), and C(5), while the five ring-carbon atoms are essentially planar. This kind of distortion is not uncommon in iridabenzene, and a recent theoretical study reveals that such distortions do not compromise the aromaticity of metallabenzene.¹⁵

In addition to the structural and spectroscopic evidence discussed above for the aromaticity of **3**, the absence of substituents at four of the ring-carbon atoms allows investigation of the reactivity of **3** toward electrophilic aromatic substitution. Bromination proceeds cleanly to give the monobrominated product $\text{Ir}[\text{C}_5\text{H}_3(\text{SMe-1})(\text{Br-4})]\text{Br}_2(\text{PPh}_3)_2$ (**4**) in high yield (see Scheme 1). This appears to be the first instance of an iridabenzene undergoing electrophilic aromatic substitution. It can be noted that bromine is introduced at the site *para* to the SMe substituent and β to the metal as expected. The same

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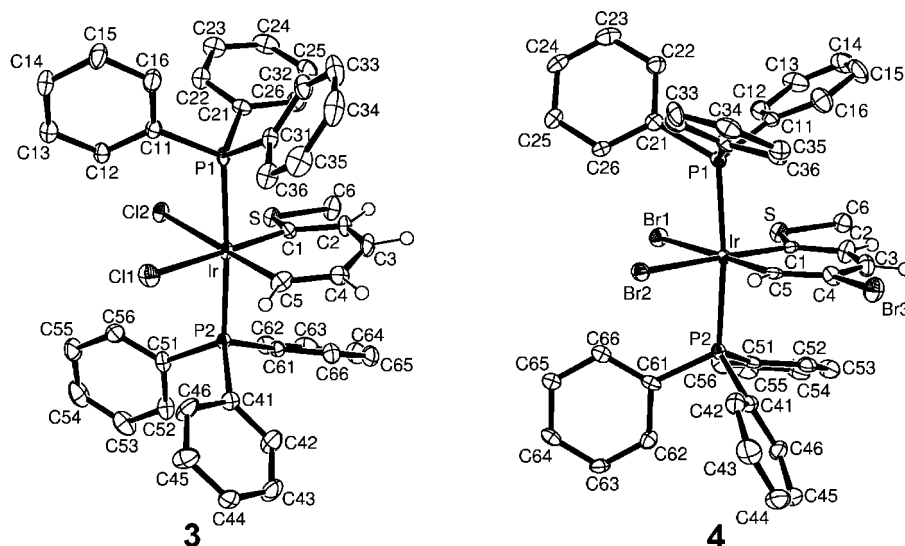


Figure 2. Molecular structure of **3** with thermal ellipsoids at the 50% probability level. Selected distances [Å]: Ir–C(1) 1.993(4), Ir–C(5) 1.992(4), C(1)–C(2) 1.427(6), C(2)–C(3) 1.363(6), C(3)–C(4) 1.413(6), C(4)–C(5) 1.352(6), Ir–Cl(1) 2.4606(11), Ir–Cl(2) 2.4846(10). The molecular structure of **4** with thermal ellipsoids at the 50% probability level. Selected distances [Å]: Ir–C(1) 2.015(7), Ir–C(5) 1.987(8), C(1)–C(2) 1.423(10), C(2)–C(3) 1.360(11), C(3)–C(4) 1.405(10), C(4)–C(5) 1.359(10), Br(3)–C(4) 1.926(7), Ir–Br(2) 2.6033(7), Ir–Br(1) 2.6130(8).

position of substitution was observed for the closely related osmabenzene $\text{Os}[\text{C}_5\text{H}_4(\text{SMe-1})(\text{Br-4})]\text{I}(\text{CO})(\text{PPh}_3)_2$.¹⁶ The crystal structure of **4**, confirming the position of bromination, is shown in Figure 2. The bond distances within the iridabenzene ring are again compatible with a delocalized system, and for this compound the iridabenzene ring is very close to planar, there being very little displacement of the Ir atom (0.0209 Å) from the least-squares C_5 plane.

Experimental Section

General Procedures and Instruments. Standard laboratory procedures were followed, as have been described previously.¹⁷ The compound $\text{IrCl}(\text{CS})(\text{PPh}_3)_2$ ¹² was prepared according to the literature methods. Infrared spectra (4000–400 cm^{-1}) were recorded as Nujol mulls between KBr plates on a Perkin-Elmer Paragon 1000 spectrometer. NMR spectra were obtained on either a Bruker DRX 400 or a Bruker Avance 300 at 25 °C. For the Bruker DRX 400, ^1H , ^{13}C , and ^{31}P NMR spectra were obtained operating at 400.1 (^1H), 100.6 (^{13}C), and 162.0 (^{31}P) MHz, respectively. For the Bruker Avance 300, ^1H , ^{13}C , and ^{31}P NMR spectra were obtained operating at 300.13 (^1H), 75.48 (^{13}C), and 121.50 (^{31}P) MHz, respectively. Resonances are quoted in ppm and ^1H NMR spectra referenced to either tetramethylsilane (0.00 ppm) or the proteo-impurity in the solvent (7.25 ppm for CHCl_3). ^{13}C NMR spectra were referenced to CDCl_3 (77.00 ppm), and ^{31}P NMR spectra to 85% orthophosphoric acid (0.00 ppm) as an external standard. Mass spectra were recorded using the fast atom bombardment technique with a Varian VG 70-SE mass spectrometer. Elemental analyses were obtained from the Microanalytical Laboratory, University of Otago.

Preparation of $[\text{Ir}(\text{CS})(\text{MeCN})(\text{PPh}_3)_2][\text{CF}_3\text{SO}_3]$ (1**).** To $\text{IrCl}(\text{CS})(\text{PPh}_3)_2$ (336 mg) in MeCN (15 mL, distilled from CaCl_2) was added AgCF_3SO_3 (110 mg). The mixture was stirred for 30 min, then filtered through Celite, and the orange solution was collected. The solvent was removed to give pure **1** as an orange solid (325 mg, 96%). m/z (FAB+): 759.11587 and 761.11637;

$\text{C}_{37}\text{H}_{30}^{191}\text{IrP}_2\text{S}$ requires 759.11495 $[\text{M} - \text{MeCN}]^+$ and $\text{C}_{37}\text{H}_{30}^{193}\text{IrP}_2\text{S}$ requires 761.11729 $[\text{M} - \text{MeCN}]^+$. Satisfactory elemental analysis could not be obtained, presumably because of the extreme sensitivity of this compound toward oxygen and moisture. IR (cm^{-1}): 2290w $\nu(\text{CN})$, 1334s $\nu(\text{CS})$. ^1H NMR (CDCl_3 , δ): 1.59 (m, MeCN, 3H), 7.51–7.56 (m, PPh_3 , 18H), 7.68–7.78 (m, PPh_3 , 12H). ^{13}C (CDCl_3 , δ): 2.01 (s, MeCN), 128.12 (s, MeCN), 128.83 (t'^{17} , $o\text{-PPh}_3$, $^2J_{\text{CP}} = 10.8$ Hz), 129.33 (t' , $i\text{-PPh}_3$, $^1J_{\text{CP}} = 56.2$ Hz), 131.54 (s, $p\text{-PPh}_3$), 134.40 (t' , $m\text{-PPh}_3$, $^3J_{\text{CP}} = 12.3$ Hz), 249.49 (br s, CS). ^{31}P (CDCl_3 , δ): 28.05.

Preparation of $[\text{Ir}(\text{C}_4\text{H}_4)\text{Cl}(\text{CS})(\text{PPh}_3)_2]$ (2**).** Ethyne was bubbled slowly through a stirred solution of a freshly prepared sample of $[\text{Ir}(\text{CS})(\text{MeCN})(\text{PPh}_3)_2][\text{CF}_3\text{SO}_3]$ (325 mg) in CH_2Cl_2 (15 mL) for 75 min. The CH_2Cl_2 was removed from the resulting green-black solution under vacuum. The resulting solid was dissolved in EtOH (15 mL), LiCl (270 mg) was added, and the solution was stirred for 2 h. During this time crude **2** precipitated as a pale brown solid. This was collected, washed with EtOH, and recrystallized twice from dichloromethane/ethanol to give pure **2** (225 mg, 65%). m/z (FAB+): 846.11573, 848.11665, and 850.11750; $\text{C}_{41}\text{H}_{34}^{35}\text{Cl}^{191}\text{IrP}_2\text{S}$ requires 846.11511 $[\text{M}^+]$, $\text{C}_{41}\text{H}_{34}^{35}\text{Cl}^{193}\text{IrP}_2\text{S}$ requires 848.11744 $[\text{M}^+]$, and $\text{C}_{41}\text{H}_{34}^{37}\text{Cl}^{193}\text{IrP}_2\text{S}$ requires 850.11449 $[\text{M}^+]$. Anal. Calc for $\text{C}_{41}\text{H}_{34}\text{ClIrP}_2\text{S} \cdot \text{CH}_2\text{Cl}_2$: C, 54.05; H 3.89. Found: C, 54.55; H, 3.72. (NMR spectroscopy showed the presence of approximately 1 molar equiv of CH_2Cl_2 of crystallization in the analytical sample.) The crystal used for X-ray structure determination was grown from dichloromethane/methanol and proved to be a methanol solvate. IR (cm^{-1}): 1297s $\nu(\text{CS})$. ^1H NMR (CDCl_3 , δ): 5.63 (m, H1 or H4 , 1H), 6.02 (m, H2 and H3 , 2H), 7.28–7.36 (m, PPh_3 , 18H), 7.39 (m, H1 or H4 , 1H), 7.67–7.75 (m, PPh_3 , 12H). ^{13}C (CDCl_3 , δ): 127.24 (t' , $o\text{-PPh}_3$, $^2J_{\text{CP}} = 10.2$ Hz), 130.03 (t' , $i\text{-PPh}_3$, $^1J_{\text{CP}} = 58.2$ Hz), 130.12 (s, $p\text{-PPh}_3$), 135.25 (t' , $m\text{-PPh}_3$, $^3J_{\text{CP}} = 10.2$ Hz), 138.50 (s, C2 or C3), 142.35 (sbr, C2 or C3), 145.13 (t, C1 or C4, $^2J_{\text{CP}} = 4.6$ Hz), 157.14 (t, C1 or C4, $^2J_{\text{CP}} = 11.8$ Hz), 284.33 (t, CS, $^2J_{\text{CP}} = 9.3$ Hz). ^{31}P (CDCl_3 , δ): –1.57.

Preparation of $[\text{Ir}[\text{C}_5\text{H}_4(\text{SMe-1})]\text{Cl}_2(\text{PPh}_3)_2]$ (3**).** Methyl triflate (48 μL , 69.6 mg) was added to a solution of $[\text{Ir}(\text{C}_4\text{H}_4)\text{Cl}(\text{CS})(\text{PPh}_3)_2]$ (72 mg) in 1,2-dichloroethane (8 mL). The solution was heated at 60 °C for 80 min. To the resulting deep red solution was added LiCl (36 mg) dissolved in n -propanol (1.5 mL), and heating at 60 °C continued for 30 min. n -Propanol (8 mL) was then added

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to the purple solution, and the 1,2-dichloroethane removed under vacuum to give crude **3** as a purple solid. Recrystallization of this from dichloromethane/ethanol gave pure **3** as purple crystals (42.8 mg, 56%). *m/z* (FAB⁺): 861.13749, 863.14100, and 865.14007; $C_{42}H_{37}^{35}Cl^{191}IrP_2S^+$ requires 861.13858 $[M - Cl]^+$, $C_{42}H_{37}^{35}Cl^{193}IrP_2S^+$ requires 863.14092 $[M - Cl]^+$, and $C_{42}H_{37}^{37}Cl^{193}IrP_2S^+$ requires 865.13797 $[M - Cl]^+$. Anal. Calc for $C_{42}H_{37}Cl_2IrP_2S$: C, 56.12; H 4.15. Found: C, 56.34; H 4.09. 1H NMR ($CDCl_3$, δ): 1.69 (s, *Me*, 3H), 6.25 (d, *H2*, $^3J_{HH} = 9.4$ Hz, 1H), 6.38 (apparent t, *H4*, $^3J_{HH} = 7.7$ Hz, 1H), 6.99 (m, *H3*, 1H), 7.22–7.31 (m, *PPh3*, 18H), 7.68–7.73 (m, *PPh3*, 12H), 12.31 (m, *H5*, 1H). ^{13}C ($CDCl_3$, δ): 21.55 (s, *Me*), 120.31 (s, *H2*), 121.64 (s, *H4*), 127.07 (t', *o-PPh3*, $^{2,4}J_{CP} = 9.7$ Hz), 129.73 (s, *p-PPh3*), 130.16 (t', *i-PPh3*, $^{1,3}J_{CP} = 55.6$ Hz), 135.29 (t', *m-PPh3*, $^{3,5}J_{CP} = 9.3$ Hz), 149.82 (s, C3), 198.19 (t, C5, $^2J_{CP} = 6.6$ Hz), 229.12 (t, C1, $^2J_{CP} = 5.2$ Hz). ^{31}P ($CDCl_3$, δ): -13.25.

Preparation of $Ir[C_5H_3(SMe-1)(Br-4)]Br_2(PPh_3)_2$ (4**).** A solution of pyridinium tribromide (46 mg) in methanol (1.5 mL) was added dropwise to a solution of $Ir[C_5H_4(SMe-1)]Cl_2(PPh_3)_2$ (43 mg) in CH_2Cl_2 (15 mL), and the mixture was stirred at rt for 45 min. Crystallization of a black product was effected by addition of methanol (15 mL) and removal of CH_2Cl_2 . This black product was redissolved in CH_2Cl_2 (15 mL), and a solution of LiBr (140 mg) in methanol (1.5 mL) was added. The mixture was stirred at rt for 15 h to complete halide substitution at iridium. The solvents were removed under vacuum until dark purple crystals were obtained. These were recrystallized from dichloromethane/ethanol to give pure **4** as dark purple crystals (44.4 mg, 87%). Anal. Calc for $C_{42}H_{36}Br_3IrP_2S$: C, 47.29; H, 3.40. Found: C, 47.09; H, 3.50. 1H NMR ($CDCl_3$, δ): 1.73 (s, *Me*, 3H), 6.35 (d, *H2*, $^3J_{HH} = 9.9$ Hz, 1H), 6.92 (dd, *H3*, $^3J_{HH} = 9.8$, $^4J_{HH} = 3.1$ Hz 1H), 7.24–7.32 (m, *PPh3*, 18H), 7.69–7.75 (m, *PPh3*, 12H), 11.86 (m, *H5*, 1H). ^{13}C ($CDCl_3$, δ): 23.19 (s, *Me*), 104.78 (s, C4), 125.68 (s, C2), 127.24 (t', *o-PPh3*, $^{2,4}J_{CP} = 9.9$ Hz), 129.98 (s, *p-PPh3*), 130.13 (t', *i-PPh3*, $^{1,3}J_{CP} = 55.8$ Hz), 135.35 (t', *m-PPh3*, $^{3,5}J_{CP} = 8.7$ Hz), 151.01 (s, C3), 186.02 (t, C5, $^2J_{CP} = 6.8$ Hz), 229.85 (t, C1, $^2J_{CP} = 5.2$ Hz). ^{31}P ($CDCl_3$, δ): -18.77.

X-ray Crystal Structure Determinations for Complexes 2–4

X-ray intensities were recorded on a Siemens SMART diffractometer with a CCD area detector using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 87 K. Data were integrated and corrected for Lorentz and polarization effects using SAINT.¹⁸ Semiempirical absorption corrections were applied based on equivalent reflections using SADABS.¹⁹ The structures were solved by direct or Patterson methods and refined by full-matrix least-squares on F^2 using the programs SHELXS97²⁰ and SHELXL97.²¹ All hydrogen atoms were located geometrically and refined using a riding model. Diagrams were produced using ORTEP3.²² For complex **2**, Squeeze²³ indicates that the crystals also contain three disordered molecules of methanol of solvation.

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Supporting Information Available: Crystal and refinement data for compounds **2–4** and crystal data in CIF format for complexes **2–4** are available free of charge via the Internet at <http://pubs.acs.org> and from the Cambridge Crystallographic Data Centre (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>) as supplementary publication nos. CCDC 646238–646240, respectively.

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