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# Synthesis and Structural Characterization of $[Ir_4(CO)_8(\eta^1\text{-}Ph)(\mu_4\text{-}\eta^3\text{-}PhPC(H)CPh)(\mu\text{-}PPh_2)]$, with a $\eta^1$-Phenyl Group Arising from Selective Cleavage of a Coordinated $Ph_2PC(H)CPh$ Ligand, and of the CO-Inserted Product $[Ir_4(CO)_8(\eta^1\text{-}C(O)Ph)(\mu_4\text{-}\eta^3\text{-}PhPC(H)CPh)(\mu\text{-}PPh_2)]$

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The $Ph_2PC(H)CPh$ ligand in $[Ir_4(CO)_9(\mu_3\text{-}\eta^3\text{-}Ph_2PC(H)CPh)(\mu\text{-}PPh_2)]$ (**1**) undergoes selective P−C bond scission upon thermolysis in toluene at 70 °C, to give $[Ir_4(CO)_8(\eta^1\text{-}Ph)(\mu_4\text{-}\eta^3\text{-}PhPC(H)CPh)(\mu\text{-}PPh_2)]$ (**2**; 60%), in addition to unreacted **1**. $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and $^1H$ NMR studies indicated the presence of two isomers in solution in a 3.2:1 ratio. The minor isomer **2b** was fully characterized by single-crystal X-ray diffraction and exhibits a flat butterfly of metal atoms, with the PhPC(H)CPh ligand interacting with all four Ir atoms. The $\eta^1$-Ph ligand is located on a wingtip Ir, on a radial site, *trans* to an Ir−Ir bond and *cis* to the P of the vinylidene ligand. A structure was proposed for the major isomer **2a**, on the basis of multinuclear NMR spectroscopy, in which the $\eta^1$-Ph ligand is located on an axial site, *trans* to the P of the vinylidene ligand. VT $^{31}P\{^1H\}$ NMR (25−90 °C) did not show interconversion of **2a** and **2b**. Carbonylation of the mixture of the two isomers yielded the CO inserted-products **3a** and **3b** (1:1.3), together with unreacted **2a**. The molecular structure of $[Ir_4(CO)_8(\eta^1\text{-}C(O)Ph)(\mu_3\text{-}\eta^3\text{-}PhPC(H)CPh)(\mu\text{-}PPh_2)]$ (isomer **3b**), established by an X-ray analysis, is similar to that of **2b**, except for the acyl group that remains bound to the same Ir atom but occupies the neighboring radial site. Multinuclear NMR studies showed that the $\eta^1$-C(O)Ph group in isomer **3a** occupies the same axial position as $\eta^1$-Ph in **2a**. A mechanism involving migration of the $\eta^1$-Ph group in **2a** and **2b**, upon carbonylation, to give **3b** and **3a**, respectively, has been proposed.

## Introduction

Chemical reactions involving cleavage of P−C bonds in phosphine, phosphide, and phosphinoacetylene ligands coordinated to transition-metal carbonyl cluster compounds are rather common processes, which are favored by the presence of adjacent metal centers and whose relative ease has been established as P−C(sp) > P−C(sp²) > P−C(sp³). The relevance of such processes to homogeneous catalytic deactivation has been discussed in a review by Garrou.[1] Studies of the thermal stability of cluster-coordinated phenyl-containing phosphorus ligands such as $PPhR_2$,[2] $PPh_2R$ (R = Me, Et),[3] $PPh_3$,[4] $Ph_2P(CH_2)_n\text{-}PPh_2$,[5] and $\mu$-$PPh_2$[6] have invariably shown that the two most favorable reactions are ortho metalation of the phenyl ring and cleavage of the P−C(Ph) bond. Though rarely isolated,[4] the σ-bonded phenyl group has been proposed to be involved in the intermediate step, in benzene reductive elimination, which is favored when a hydride ligand is available in the cluster,[7] biphenyl reductive elimination,[8] and even migratory CO insertion to give the acyl group C(O)Ph,[9] in the absence of any hydride.

We recently reported that reaction of $[Ir_4(CO)_{10}(\mu\text{-}PPh_2)]^-$ with $Ph_2PCCPh$, followed by protonation, leads to the formation of $[Ir_4(CO)_9(\mu_3\text{-}\eta^3\text{-}Ph_2PC(H)CPh)(\mu\text{-}PPh_2)]$ (**1**) and $[HIr_4(CO)_9(\mu_4\text{-}\eta^3\text{-}Ph_2PCCPh)(\mu\text{-}PPh_2)]$, as a result of protonation at the $Ph_2PCCPh$ ligand and at

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the metal frame, respectively.[10] In this report, we describe our studies involving the selective cleavage of a P−C(Ph) bond in **1** to yield the two structural isomers **2a** and **2b** of the new compound $[Ir_4(CO)_8(\eta^1\text{-}Ph)(\mu_3\text{-}\eta^3\text{-}PhPC(H)CPh)(\mu\text{-}PPh_2)]$. Studies of the carbonylation of **2a** and **2b** were also undertaken, for comparison with the carbonylation of the related methyl species $[Ir_4(CO)_8(CH_3)(\mu_4\text{-}\eta^3\text{-}Ph_2PCCPh)(\mu\text{-}PPh_2)]$.[11] The acyl products $[Ir_4(CO)_8(\eta^1\text{-}C(O)Ph)(\mu_3\text{-}\eta^3\text{-}PhPC(H)CPh)(\mu\text{-}PPh_2)]$ (**3a**,**b**) were proposed to be formed as a result of the migration of the $\eta^1$-Ph ligand in **2b** and **2a**, respectively, to a neighboring CO ligand. To our knowledge, this is the first study involving the carbonylation of a phenyl group coordinated to a metal cluster.

## Results and Discussion

Thermolysis of the bright yellow compound $[Ir_4(CO)_9(\mu_3\text{-}\eta^3\text{-}Ph_2PC(H)CPh)(\mu\text{-}PPh_2)]$ (**1**) in toluene at 80 °C for 48 h resulted in a purple solution, from which dark purple $[Ir_4(CO)_8(\eta^1\text{-}Ph)(\mu_4\text{-}\eta^3\text{-}PhPC(H)CPh)(\mu\text{-}PPh_2)]$ (**2**) was obtained in up to 60% yield, after purification by TLC, in addition to unreacted **1** and decomposition products. Heating for longer periods of time only resulted in additional decomposition. Attempts at inducing the formation of **2** by reacting **1** with $Me_3NO$ at −40 °C also led to decomposition.

Compound **2** was formulated on the basis of analytical and spectroscopic data discussed below. $^1H$, $^{13}C$, and $^{31}P\{^1H\}$ NMR studies indicated that it exists in two distinct isomeric forms, **2a** and **2b**, in an approximate 3.2:1 ratio. Exhaustive attempts at separating these two species by HPLC[12] using a variety of solvent systems were unsuccessful. Crystallization from $CH_2Cl_2$/hexane and from THF produced crystalline materials whose $^{31}P\{^1H\}$ NMR spectra were identical with those of the solid obtained after purification by TLC. Suitable crystals for X-ray analysis, obtained from a THF solution of the two isomers at −5 °C, were later established to be of isomer **2b**.

**Crystal Structure of 2b**. The molecular structure of **2b** in the solid state is shown in Figure 1, together with the atomic labeling scheme. Relevant structural parameters are shown in Table 1. The metal framework constitutes a flat butterfly (maximum deviation from the mean Ir atom plane 0.9 Å). Metal−metal bond distances range from 2.650(1) to 2.934(1) Å, the longest bond being the butterfly hinge. Eight CO ligands are terminally bound, two on each iridium atom; four CO's are bound in radial positions with respect to the metal frame, while the remaining four CO's adopt an axial coordination. The Ir(1)−Ir(4) edge is spanned by the diphenylphosphido ligand (Ir(1)−P(2) = 2.272(3) and Ir(4)−P(2) = 2.337(3) Å), which donates three electrons to the cluster. The PhPC(H)CPh ligand interacts with all four iridium atoms, formally contributing a total of six electrons to the cluster *via* the three-electron P−Ir bridging interaction (P(1)−Ir(3) = 2.297(3) and P(1)−Ir(4) = 2.299(2) Å) and one $\pi$- and one $\sigma$-interaction from the ethylenic system (C(9)−Ir(2) = 2.22(1), C(10)−Ir(2) = 2.26(1), C(10)−Ir(1) = 2.06 Å for the $\pi$- and $\sigma$-bonds, respectively). The bonding pattern within the PhCC(H) system is in agreement with the description of the

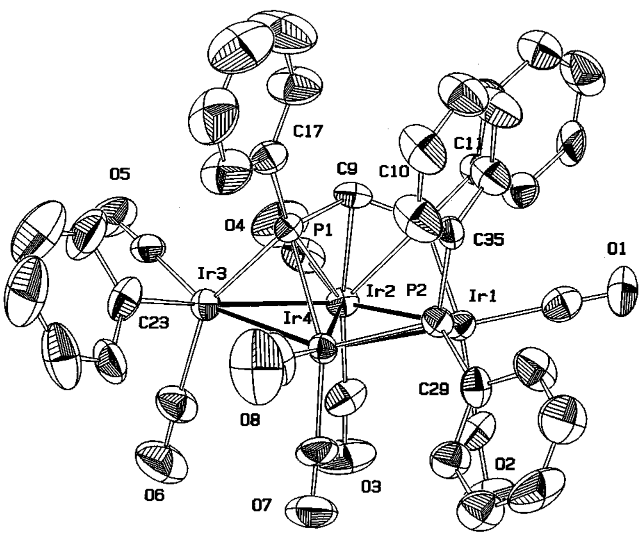

**Figure 1.** Molecular structure of $[Ir_4(CO)_8(\eta^1\text{-}Ph)(\mu_4\text{-}\eta^3\text{-}PhPC(H)CPh)(\mu\text{-}PPh_2)]$ (**2b**).

**Table 1. Selected Bond Distances (Å) and Angles (deg) for 2b and 3b**

| | 2b | 3b |
|---|---|---|
| Ir(1)−Ir(2) | 2.6515(8) | 2.668(1) |
| Ir(1)−Ir(4) | 2.8560(8) | 2.845(1) |
| Ir(2)−Ir(3) | 2.7758(8) | 2.731(1) |
| Ir(2)−Ir(4) | 2.9348(7) | 2.845(1) |
| Ir(3)−Ir(4) | 2.7664(8) | 2.854(1) |
| Ir(3)−P(1) | 2.300(3) | 2.287(4) |
| Ir(4)−P(1) | 2.300(3) | 2.311(4) |
| Ir(1)−P(2) | 2.271(3) | 2.276(4) |
| Ir(4)−P(2) | 2.334(3) | 2.317(5) |
| C(99)−C(23) | | 1.52(2) |
| C(99)−O(99) | | 1.19(2) |
| mean $Ir-C_{CO}$ | 1.89(1) | 1.91(2) |
| mean C−O | 1.14(1) | 1.11(2) |
| Ir(2)−C(9) | 2.22(1) | 2.24(2) |
| Ir(1)−C(10) | 2.06(1) | 2.08(2) |
| Ir(2)−C(10) | 2.26(1) | 2.28(2) |
| Ir(3)−C(23) | 2.09(1) | |
| Ir(3)−C(99) | | 2.10(2) |
| P(1)−C(9) | 1.79(1) | 1.77(2) |
| P(1)−C(17) | 1.80(1) | 1.81(2) |
| P(2)−C(29) | 1.81(1) | 1.84(2) |
| P(2)−C(35) | 1.82(1) | 1.82(2) |
| C(9)−C(10) | 1.42(2) | 1.42(2) |
| C(10)−C(11) | 1.49(1) | 1.49(2) |
| mean $C_{phenyl}-C_{phenyl}$ | 1.37(2) | 1.37((3) |
| Ir(2)−Ir(1)−Ir(4) | 64.27(2) | 62.05(3) |
| Ir(1)−Ir(2)−Ir(3) | 118.63(2) | 122.28(3) |
| Ir(4)−Ir(3)−Ir(2) | 63.95(2) | 61.20(3) |
| Ir(3)−Ir(4)−Ir(1) | 112.23(2) | 112.13(3) |
| Ir(4)−(P1)−Ir(3) | 73.94(8) | 76.8(1) |
| Ir(4)−P(2)−Ir(1) | 76.65(9) | 76.5(1) |
| C(10)−C(9)−P(1) | 127.4(8) | 126(1) |
| C(9)−C(10)−C(11) | 116.3(9) | 115(1) |
| C(9)−C(10)−Ir(1) | 123.3(7) | 125(1) |
| C(11)−C(10)−Ir(1) | 120.4(7) | 120(1) |
| C(11)−C(10)−Ir(2) | 129.4(7) | 127(1) |
| P(1)−Ir(3)−C(99) | | 99.4(5) |
| P(1)−Ir(3)−C923) | 95.5(4) | |
| C(99)−Ir(3)−Ir(4) | | 147.2(5) |
| C923)−Ir(3)−Ir(2) | 160.8(3) | |

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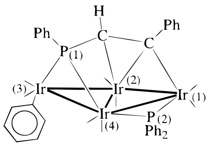
ligand−cluster interaction. The C(9)−C(10) distance (1.42(1) Å) and the Ir(1)−C(10)-C(9) and P(1)−C(9)−C(10) angular values (123(1) and 127(1)°, respectively) are indicative of two $sp^2$-hybridized C atoms. The phenyl ligand is bonded terminally to a wingtip Ir atom (C(23)−Ir(3) = 2.10(1) Å), *trans* to the Ir(3)−Ir(2) bond (2.7758(8) Å, C(23)−Ir(3)−Ir(2) = 160.8(3)°) and *cis* to P(1) (C(23)−Ir(3)−P(1) = 95.5(4)°); the C−Ir bond distance compares well with that observed for the compound $[Ir_3(CO)_6(\eta^1\text{-}Ph)(\mu_3\text{-}PPh)(dppm)]$ (C(8)−Ir(1) = 2.08 Å), which is formed as a result of P−C(Ph) bond cleavage in $CH(PPh_2)_3$ in the presence of $[IrCl(CO)_2(CH_3C_6H_4NH_2\text{-}p)]$ and Zn under CO[13] and is the only other Ir cluster known to possess an $\eta^1$-Ph group.

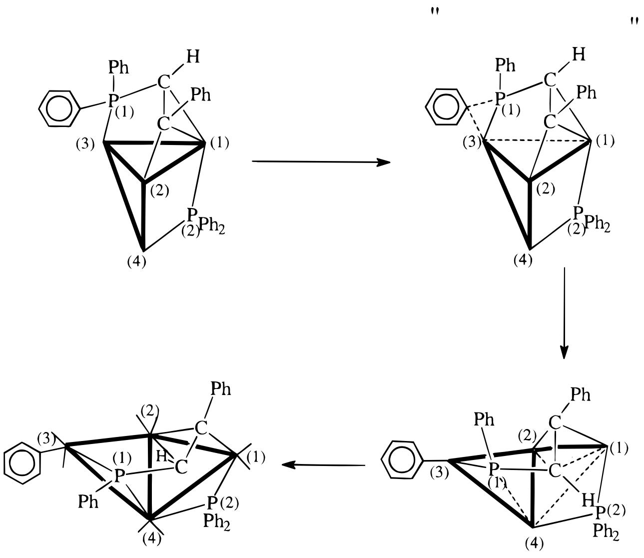
**Solution Structures of 2a and 2b.** The $^1$H NMR spectrum of the mixture containing **2a** and **2b** consists of two multiplets at $\delta$ 7.80−6.85 and 6.72−6.60 of approximate relative intensities 3:1, attributed to the Ph hydrogens of the P- and Ir-bonded groups, respectively, and two doublets at $\delta$ 6.50 and 5.70 with $J_{P-H}$ = 20 Hz, of relative intensities 3.2:1, assigned to the vinyl hydrogens of the PhPC(H)CPh ligand in the two isomers. The $^{31}P\{^1H\}$ NMR spectrum shows two sets of doublets with approximate relative intensities of 3.2:1 at $\delta$ 118.0 and 83.0 and at $\delta$ 145.0 and 61.0, with the same $J_{P-P}$ = 8 Hz, suggesting that the two isomers have very similar structures, with small differences in the Ir−Ir bonds bridged by the phosphido groups.[14] The spectrum in $d_8$-toluene remains unchanged from 25 to 90 °C, indicating that these species do not interconvert under these conditions. The similarity of the two structures was confirmed by the observation of almost identical chemical shifts for carbons C(9) and C(10) of **2a** and **2b** in the $^{13}C\{^1H\}$ NMR spectrum. The two singlets at $\delta$ 123.6 and 123.4 (∼3.5:1), the singlet at $\delta$ 143.7, and the doublet at $\delta$ 143.1 with $J_{P-C}$ = 5Hz (∼3.5:1) were attributed unequivocally to C(10) and C(9) of isomers **2a** and **2b**, respectively, on the basis of a C−H correlation spectrum. Finally, the P−H correlation spectrum indicated that the structure determined in the solid state is that of compound **2b**. Indeed, it showed that P(1) of the major isomer **2a**, which appears at $\delta$ 88.3, couples with the vinyl proton at $\delta$ 6.50, with the protons of the Ph group to which it is bound, and with the protons of the $\eta^1$-Ph at $\delta$ 6.72−6.60, while in the case of compound **2b**, the spectrum did not show any interaction between P(1) at $\delta$ 61.0 and the protons of the $\eta^1$-Ph group.



2a

On the basis of these data, a structure was proposed for isomer **2a** that differs from that of **2b** in that the $\eta^1$-Ph ligand occupies an axial position on Ir(3), *trans* to P(1), which gives rise to the $P-H_{Ph}$ interaction seen in the P−H correlation spectrum, while in **2b** $\eta^1$-Ph occupies one of the radial positions, *cis* to P(1). It is interesting to note that compounds $[L(CO)_3Ru(\mu\text{-}PPh_2)Co(CO)_3]$ (L = phosphines) also exist in solution as isomers arising from the *cis* and *trans* dispositions of the phosphine coordinated to ruthenium with respect to the phosphido bridge.[15] In these compounds, shifts of about 12−20 ppm in $\delta(\mu\text{-}PPh_2)$ were observed, depending on whether L was *trans* or *cis* to the M−M bond. Shifts of the same magnitude were noted in the case of isomers **2a** and **2b**, surprisingly, for both phosphido groups $\mu$-$PPh_2$ and $\mu$-PPhC(H)CPh, which indicates that the electronic effects of the $\eta^1$-Ph group on the Ir(3) atom are carried through the molecule to the $\mu$-$PPh_2$ ligand. In contrast with the *cis* and *trans* isomers of compounds $[L(CO)_3Ru(\mu\text{-}PPh_2)Co(CO)_3]$, which undergo interconversion in solution at room temperature, isomers **2a** and **2b** do not interconvert.

**Scheme 1**



**Speculations on the Mechanism of Formation of 2a and 2b.** The selectivity of the process involving the formation of **2a** and **2b** is noteworthy, considering the conditions of the reaction and the number of possible activation sites in compound **1**. A close look at the molecular structure of $[Ir_4(CO)_8(PCy_3)(\mu_3\text{-}\eta^3\text{-}Ph_2PC(H)CPh)(\mu\text{-}PPh_2)]$ (**1a**), which possesses the same structure as **1** (see Scheme 1), except for the presence of the $PCy_3$ ligand,[10] suggests that this selectivity might be associated with the fact that the $P(1)-C_{Ph}$ bond of the $Ph_2PC(H)CPh$ group is oriented toward Ir(3), which might facilitate the formation of an activated state for the oxidative-addition process. A similar situation was evident in the case of the activation of the $P-C_{Ph}$ bond in $[HRu_3(CO)_{10}(\mu\text{-}PPh_2)]$.[16] A free coordination site for the oxidative addition of the P−C bond could result from either the loss of a CO or cleavage of an Ir−Ir bond. Significantly, attempts at using $Me_3NO$ to induce the transformation of **1** to **2** only led to the decomposition of **1**. It is interesting to note that the monosubstitution of CO in **1** with L (L = $PCy_3$, $P(OMe)_3$) has been shown to occur, under conditions much milder than those employed for this transformation, exclusively on Ir(4), which does not interact with the $\mu_3$-$\eta^3$-$Ph_2PC(H)CPh$

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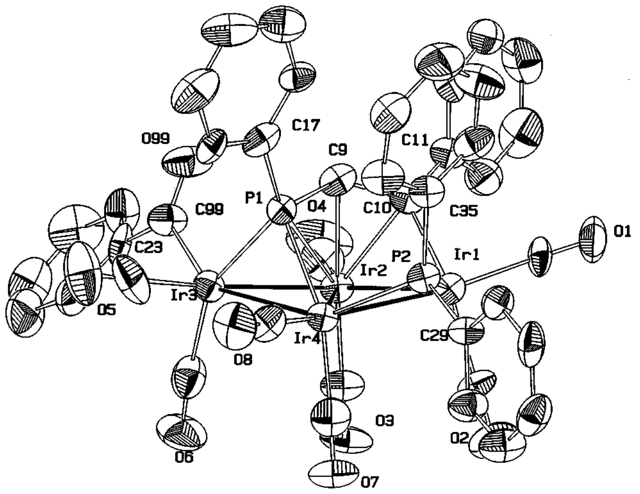


**Figure 2.** Molecular structure of [$Ir_4(CO)_8(\eta^1\text{-}C(O)Ph)(\mu_4\text{-}\eta^3\text{-}PhPC(H)CPh)(\mu\text{-}PPh_2)$] (**3b**).

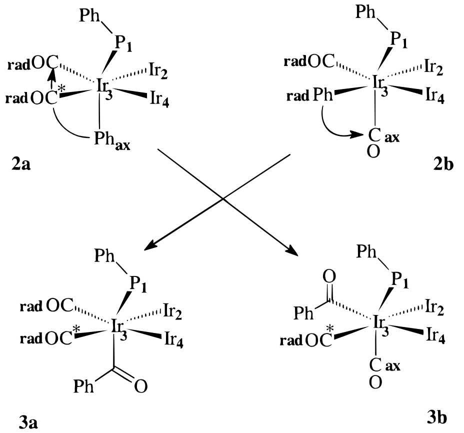
ligand.[10] The transformation of **1** into **2** can be visualized in Scheme 1, presuming that the $\mu$-PPh$_2$ group does not undergo migration.

**Reaction of 2a and 2b with CO**. The isomeric mixture containing **2a** and **2b**, in THF, reacted with CO under forcing conditions (70 °C and 72 h), to give the CO-inserted products [$Ir_4(CO)_8(\eta^1\text{-}C(O)Ph)(\mu_4\text{-}\eta^3\text{-}PhPC(H)CPh)(\mu\text{-}PPh_2)$] (**3a**,**b**). The reaction was monitored by $^{31}P\{^1H\}$ NMR which showed the appearance of two new sets of doublets that were attributed to the $\mu$-PPh$_2$ and $\mu_4$-$\eta^3$-PhPC(H)CPh phosphorus nuclei of isomer **3a**, at $\delta$ 123.2 and 89.4 ($J_{P-P} = 11$ Hz), respectively, and of isomer **3b**, at $\delta$ 157.9 and 56.3 ($J_{P-P} = 8$ Hz), respectively, by analogy with the spectrum of the **2a**,**b** mixture. The negligible differences in the chemical shifts of about 4−12 ppm, compared to those observed for **2a** and **2b**, indicated that very small changes in the cluster frameworks occurred upon CO insertion. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture after 72 h showed that there was an approximate **3a**:**3b** ratio of 1:1.3 and that all of **2b** had reacted. Purification by TLC, at this stage, gave **3a**,**b** in 70% yield, together with unreacted **2a** (30%). Attempts at growing suitable crystals of **2a** for an X-ray analysis, from a solution of pure **2a**, were unsuccessful.

The patterns of the IR absorbances of the **2a**,**b** and **3a**,**b** mixtures were similar, except for the $\nu_{CO}$ signal of the acyl ligand at 1626 cm$^{-1}$ in the spectrum of the $\eta^1$-C(O)Ph compounds. The $^1H$ NMR spectra of the two isomeric mixtures were also very similar, except for the relative intensities of the vinyl protons, which were approximately 1:1.3 and 3.2:1 in the $\eta^1$-C(O)Ph and $\eta^1$-Ph compounds, respectively. The mixture **3a**,**b** crystallized from hexane at 15 °C, and crystals suitable for an X-ray experiment, later shown to be of isomer **3b**, were isolated.

**Crystal Structure of 3b**. The structure of **3b** in the solid state is very similar to that of **2b** discussed above (see Figure 2). Relevant structural parameters are compared to those of **2b** in Table 1. Indeed, the major structural difference resides in the ligand distribution around atom Ir(3). While the phenyl ring in **2b** is radially bound to the cluster *trans* to the Ir(3)−Ir(2) bond (C(23)−Ir(3)−Ir(2) = 160.8(3)°), in **3b** the C(O)Ph ligand generated by CO insertion into the Ir−C$_{Ph}$ bond is *transoid* to the Ir(3)-Ir(4) bond (C(99)−Ir(3)−Ir(4) = 147.2(5)°), where Ir(4) is one of the atoms involved in the diphenylphosphido bridge. The Ph and C(O)Ph ligands are *cis* to the P(1) atom (C(23)−Ir(3)−P(1) = 95.5(4)° and C(99)−Ir(3)−P(1) = 99.4(5)°) in **2b** and **3b**, respectively. Ir−Ir bond distances range from 2.6680(14) to 2.8544(13) Å, the longest bond being Ir(3)−Ir(4) *trans* to the C(O)Ph ligand, while the butterfly hinge is intermediate (2.8454(11) Å). As in **2b**, the Ir(1)−Ir(4) edge is spanned by the diphenylphosphido ligand (Ir(1)−P(2) = 2.276(4) Å and Ir(4)−P(2) = 2.317(5) Å). The structural parameters within the PhPC(H)CPh ligand conform to the values found for **2b**: P(1)−Ir(3) = 2.287(4) Å, P(1)−Ir(4) = 2.311(4) Å, C(9)−Ir(2) = 2.24(2) Å, C(10)−Ir(2) = 2.28(2) Å, C(10)−Ir(1) = 2.08(2) Å, and C(9)−C(10) = 1.42(2) Å. The Ir−C distance involving the C(O)Ph ligand (C(99)−Ir(3) = 2.10(1) Å) is the same as the corresponding distance in **2b**, while the C═O separation is 1.19(2) Å. The Ir(3)−C(99)−C(23) angle of 123.6(13)° corresponds to an sp$^2$-hybridized atom.

**Scheme 2**



**CO Insertion Process.** Spectroscopic data confirm that the $\eta^1$-C(O)Ph group in **3a** occupies the same axial position as in **2a**. However, the fact that the $\eta^1$-Ph and $\eta^1$-C(O)Ph ligands in **2b** and **3b**, respectively, occupy adjacent radial positions might suggest that the process involves migration of the Ph group, rather than CO insertion. As illustrated in Scheme 2, migration of radial $\eta^1$-Ph in **2b** to axial CO would give **3a**, and that of axial $\eta^1$-Ph in **2a** to radial CO *trans* to the Ir(3)−Ir(4) bond would give **3b**. Inspection of the molecular structure of **2b** (Figure 1) suggests that the alternative migration paths of $\eta^1$-Ph in **2a** and **2b** might be sterically hindered by the Ph group on P(1). A mechanism involving the equilibration of these species under CO pressure cannot be excluded, even though neither compounds **2a** and **2b** nor compounds **3a** and **3b** undergo interconversion at the temperature of the CO insertion reaction in the absence of CO, as shown by $^{31}P\{^1H\}$ NMR spectroscopy.

To our knowledge, this is the first report of a carbonylation reaction of a metal cluster compound containing a M−C$_{aryl}$ or M−C$_{alkyl}$ bond for which a mechanism involving migration of the aryl group to give the acyl derivative has been proposed, although in the case of mononuclear species, this is a textbook process.[17] It is interesting that the rates of CO insertion of compounds

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(17) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. In *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

**2a**,**b** are much slower than that found for the related compound $[Ir_4(CO)_8(Me)(\mu_4\text{-}\eta^3\text{-}Ph_2PCCPh)(\mu\text{-}PPh_2)]$ (**4**), whose reaction with CO (1 atm, 40 °C, 7 h, 100%) gives the isostructural $[Ir_4(CO)_8(C(O)Me)(\mu_4\text{-}\eta^3\text{-}Ph_2PCCPh)(\mu\text{-}PPh_2)]$, *via* a CO addition intermediate, detected both visually and spectroscopically.[11] Although this relative reluctance of **2a**,**b** to react with CO, compared with the case for **4**, might be associated with the differences in their structures, it is in accordance with the trend observed in the rates of CO migratory insertions in mononuclear compounds. For example, greater aptitude of the Me versus Ph migration has been observed in Rh(III)[18] and Ir(III)[19] compounds.

## Experimental Section

All manipulations and reactions were carried out under dry argon, unless otherwise specified, using standard Schlenk techniques. $CH_2Cl_2$ was dried over $CaH_2$, hexane and toluene were dried over sodium, and ethyl acetate was dried over $P_2O_5$. Solvents were freshly distilled under argon and freed from dissolved oxygen, where compatible, by freeze-degassing before use. $Me_3NO$ (Aldrich) was sublimed before use, and $[Ir_4(CO)_9(\mu_3\text{-}\eta^3\text{-}Ph_2PC(H)CPh)(\mu\text{-}PPh_2)]$[10] was prepared by a literature method.

Preparative TLC was carried out in air by using ca. 2 mm thickness glass-backed silica plates (20 × 20 cm) prepared from silica gel type GF 254 (Fluka) and ethyl acetate−hexane (1:5) as eluent, unless otherwise specified, and the compounds were extracted from the silica with dichloromethane. The following eluents were used in attempts at separating isomers **2a** and **2b** by TLC: $CH_2Cl_2$−hexane (from 1:2 to 1:9) and ethyl acetate−hexane (from 1:4 to 1:9).

The separation of isomers **2a** and **2b** was attempted by HPLC,[12] by injecting 15 $\mu$L samples of a $CH_2Cl_2$ solution of **2** (2 $\mu$g/mL) on an HP1090 series II M chromatograph with a variable-wavelength UV−vis detector ($\lambda$ = 254 nm). The flow rate was 1.0 mL/min. Elution on a Lichrospher Si-60 5 $\mu$m, 4 × 125 mm (normal phase) column, using $CH_2Cl_2$−hexane mixtures that started from pure hexane up to a 1:1 mixture, or on a $\mu$Bondapac CK, C18−10 $\mu$m, 3.9 × 3000 mm (reverse phase) column, using methanol−ethyl acetate mixtures that started from pure methanol up to a 1:1 mixture, did not lead to separation.

IR spectra were obtained on a Bomem MB series IR instrument scanning between 2200 and 1500 cm$^{-1}$, using $CaF_2$ cells. $^1H$, $^{13}C$, and $^{31}P\{^1H\}$ NMR data were obtained on a Bruker AC 300/P instrument using deuterated solvents as lock and reference ($^1H$ and $^{13}C$, $SiMe_4$; $^{31}P$, 85% $H_3PO_4$ (external)). The long-range $^{31}P-^1H$ and $^{13}C-^1H$ correlation spectra of the mixture of compounds **2a** and **2b** were obtained using the COLOC sequence with $J_{P-H}$ = 20 and $J_{C-H}$ = 4 Hz, respectively. Microanalyses were performed at the Instituto de Química Unicamp, Campinas, Brazil.

**Preparation of $[Ir_4(CO)_8(\eta^1\text{-}Ph)(\mu_4\text{-}\eta^3\text{-}PhPC(H)CPh)(\mu\text{-}PPh_2)]$ (2).** Compound **1** (60.0 mg, 0.040 mmol) was heated in toluene (40 mL) at 80 °C for 48 h. The solvent was evaporated and the residue dissolved in $CH_2Cl_2$; TLC of the purple solution gave, besides unreacted **1** (10.0 mg, 25%), purple compound **2** (36.0 mg, 60%; $R_f$ = 0.60). Crystallization from THF at −5 °C or from dichloromethane−hexane (1:3) at various temperatures led to crystalline materials whose $^{31}P$ NMR spectra were identical with that of the solid obtained from TLC. Anal. Calcd for $C_{40}H_{26}O_8P_2Ir_4$: C, 32.8; H, 1.8. Found: C, 32.8; H, 1.8. IR (hexane, cm$^{-1}$): $\nu_{CO}$ 2070 s, 2038 s, 2014 m, 1993 wbr, 1975 w, 1962 w. $^1H$ NMR, ($CDCl_3$): $\delta$ 5.70 (d, H (**2b**), $J_{H-P}$ = 20 Hz) 6.50 (d, H (**2a**), $J_{H-P}$ = 20 Hz), 6.60−6.72 (m, $\eta^1\text{-}C_6H_5$), 6.85−7.80 (m, Ph). $^{13}C$ NMR ($CD_2Cl_2$): $\delta$ 123.4 [s, $C_{Ph}$ (**2b**)], 123.6 [s, $C_{Ph}$ (**2a**)], 143.1 [d, $C_H$ (**2b**), $J_{P-C}$ = 5 Hz], 143.7 [s, $C_H$ (**2a**)], 127.8−132.5 (m, Ph).

**Table 2. Crystal Data and Details of Measurements for 2b and 3b**

| | 2b | 3b |
|---|---|---|
| formula | $C_{40}H_{26}Ir_4O_8P_2$ | $C_{41}H_{26}Ir_4O_9P_2$ |
| mol wt | 1465.2 | 1493.36 |
| system | triclinic | triclinic |
| space group | $P\bar{1}$ | $P\bar{1}$ |
| $a$ (Å) | 12.219(2) | 13.430(3) |
| $b$ (Å) | 12.893(2) | 13.450(3) |
| $c$ (Å) | 13.007(2) | 12.707(6) |
| $\alpha$ (deg) | 95.136(5) | 103.34(3) |
| $\beta$ (deg) | 101.61(1) | 101.79(3) |
| $\gamma$ (deg) | 91.18(1) | 64.98(2) |
| $V$ (Å$^3$) | 1997.6(5) | 2009(1) |
| $Z$ | 2 | 2 |
| $F$(000) | 1336 | 1364 |
| $\lambda$(Mo K$\alpha$) (Å) | 0.710 69 | 0.710 69 |
| $\mu$(Mo K$\alpha$) (mm$^{-1}$) | 13.41 | 13.37 |
| $\theta$ range (deg) | 2.5−25 | 3.0−25 |
| octants explored ($h_{min}/h_{max}$, $k_{min}/k_{max}$, $l_{min}/l_{max}$) | −14/14, −15/15, 0/15 | −15/15, −15/15, 0/15 |
| no. of measd rflns | 9230 | 9456 |
| no. of unique rflns | 6207 | 7039 |
| no. of refined params | 487 | 505 |
| GOF on $F^2$ | 1.220 | 1.018 |
| R1 (on $F$, $I > 2\sigma(I)$) | 0.0338 | 0.053 |
| wR2 (on $F^2$, all data) | 0.1350 | 0.1602 |

Attempts at improving the yields of **2** were unsuccessful. Heating **1** to 80 °C, but for 72 h instead of 48 h, led to lower yields of **2** and to the decomposition of **1**, and heating to 90 °C for 48 h resulted in a decrease in the yield of **2** (<10%) and in the formation of several other products in low yields, besides heavy decomposition.

**Reaction of 1 with $Me_3NO$.** To a yellow solution of **1** (20.0 mg, 0.013 mmol) in $CH_2Cl_2$ (8 mL) cooled to −40 °C was added a freshly made 0.134 mmol/10 mL $CH_2Cl_2$ solution of $Me_3NO$ (1 mL, 0.013 mmol), and the resulting mixture was warmed slowly to room temperature. IR spectroscopy and TLC indicated that decomposition had occurred.

**Reaction of $[Ir_4(CO)_8(\eta^1\text{-}Ph)(\mu_4\text{-}\eta^3\text{-}PhPC(H)CPh)(\mu\text{-}PPh_2)]$ (2) with CO.** CO was bubbled through a solution of **2** (40.0 mg, 0.028 mmol) in THF (30 mL) for 15 min at −40 °C. The Schlenk tube bearing a J. Young vaccuum stopcock was then sealed under a positive pressure of CO and the mixture heated to 70 °C for 36 and 72 h. The solvent was evaporated under reduced pressure and the residue dissolved in $CDCl_3$ for $^{31}P\{^1H\}$ NMR monitoring. The residue of the 72 h reaction was separated by TLC to give unreacted **2** ($R_f$ = 0.60) and $[Ir_4(CO)_8(\eta^1\text{-}C(O)Ph)(\mu_4\text{-}\eta^3\text{-}PhPC(H)CPh)(\mu\text{-}PPh_2)]$ (**3**; 28.0 mg, 70%; $R_f$ 0.50). Anal. Calcd for $C_{41}H_{26}O_9P_2Ir_4$: C, 33.0; H, 1.7. Found: C, 34.0; H, 1.7. IR (hexane, cm$^{-1}$): $\nu_{CO}$ 2072 m, 2038 s, 2016 m, 1993 wbr, 1626 w cm$^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 5.50 [d, H(**3b**), $J_{H-P}$ = 18 Hz], 6.58 [d, H(**3a**), $J_{H-P}$ = 20 Hz], 6.60−7.10 (m, $\eta^1\text{-}C_6H_5$), 7.20−7.60 (m, Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$): **3a**, $\delta$ 123.2 (d, $PPh_2$, $J_{P-P}$ = 11 Hz), 89.4 (d, PhPC(H)CPh); **3b**, $\delta$ 157.9 (d, $PPh_2$, $J_{P-P}$ = 8 Hz), 56.3 (d, PhPC(H)CPh).

**Crystal Structure Characterization.** Diffraction data collections for **2b** and **3b** were carried out on an Enraf-Nonius CAD4. Details of data collection and measurements are provided in Table 2. SHELX86 and SHELXL93[20] were used for data treatment and refinement based on $F^2$. Absorption correction was applied by the Walker and Stuart method[21] (correction range 0.72−1.00 for **2b** and 0.76−1.00 for **3b**). All non-H atoms were allowed to vibrate anisotropically. H atoms

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(21) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. B* **1983**, *39*, 158.

were added in calculated positions (C−H = 0.93 Å) and refined "riding" on the corresponding C atoms. Tables giving additional details of measurements and refinement, atomic coordinates, thermal parameters, and all bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. SCHAKAL92[22] was used for the graphic representation of the results.

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**Supporting Information Available:** Complete listings of fractional atomic coordinates, anisotropic thermal parameters, fractional atomic coordinates for the H atoms, and bond lengths and angles for **2b** and **3b** (18 pages). Ordering information is given on any current masthead page.

OM9609731

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