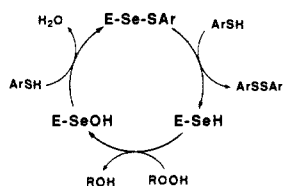


**Figure 1.** Lineweaver–Burk plots for reduction of *tert*-butyl hydroperoxide by 3-carboxy-4-nitrobenzenethiol catalyzed by selenosubtilisin (ESeSAr form) at 25.0 °C and pH 5.5 (100 mM MES buffer, 1 mM EDTA). The initial rates of the reaction were measured at 60  $\mu\text{M}$  (○), 120  $\mu\text{M}$  (●), and 400  $\mu\text{M}$  (■) thiol **1**, respectively, by monitoring the disappearance of thiol at 412 nm. Enzyme concentration was determined by BCA titration using native subtilisin as a standard.<sup>12</sup>

#### Scheme I



originally proposed for glutathione peroxidase.<sup>2</sup> If this mechanism is correct, it should be possible to trap free selenol. Indeed, we found that treating the enzyme with excess iodoacetate in the presence of thiol results in complete loss of catalytic activity.<sup>10</sup>

To gauge the catalytic efficiency of selenosubtilisin, we compared the enzyme with diphenyl diselenide, a well-studied antioxidant.<sup>11</sup> At 25.0 °C and pH 5.5, the initial rate for the reduction of *t*-BuOOH (250  $\mu\text{M}$ ) by thiol **1** (100  $\mu\text{M}$ ) in the presence of 1  $\mu\text{M}$  enzyme (ESeSAr form) is  $1.5 \times 10^{-6}$  M/min. Under similar conditions, but with 7.5 mM PhSeSePh as the catalyst, the initial rate is only  $1.6 \times 10^{-7}$  M/min. Thus, the protein binding site confers a rate advantage of at least 70 000-fold to the artificial enzyme over diphenyl diselenide.

In short, we have shown that a semisynthetic selenium-containing enzyme catalyzes the reduction of *tert*-butyl hydroperoxide by an aryl thiol with much higher chemical efficiency than does a model selenium compound. Since the enzymatic reaction is mechanistically similar to the redox chemistry of glutathione peroxidase, further characterization of selenosubtilisin may lead to a better understanding of the natural system. Such information will be invaluable for the rational design of selenium-based antioxidants and practical redox catalysts.

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(10) Selenosubtilisin (ESeSAr form, 500  $\mu\text{M}$ ) was incubated with iodoacetic acid (50 mM) and treated successively with three portions of thiol **1** (5 mM) for 10 min each at room temperature and pH 5.0. Enzyme that was recovered after gel filtration on G-25 had no detectable redox activity. Enzyme similarly treated with iodoacetic acid but in the absence of thiol was recovered with full activity. For an analogous experiment with glutathione peroxidase, see: Forstrom, J. W.; Zakowski, J. J.; Tappel, A. L. *Biochemistry* **1978**, *17*, 2639.

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## Metal-Promoted Binuclear C–H Activation of Ethylene and Formation of a Novel Heterobimetallic Ir–Pt Complex. X-ray Crystal Structure of $[(\text{Ph}_3\text{P})_2(\text{CO})\text{Ir}(\mu\text{-H})(\mu\text{-}\eta^2\text{:}\eta^1\text{-CH=CH}_2)\text{Pt}(\text{PPh}_3)_2]^+\text{CF}_3\text{SO}_3^-$

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Heterobimetallic complexes containing asymmetric metal–metal bonds<sup>1</sup> as well as homogeneous C–H bond activation<sup>2</sup> by organometallic compounds are of considerable current interest largely because of their relevance to catalysis.<sup>3</sup> Although coordination of an alkene to transition metal systems is generally considered a necessary activation step in many catalytic and stoichiometric organometallic reactions,<sup>4</sup> little is known about alkene C–H bond activation<sup>2</sup> of precomplexed olefin substrates. In this paper we report the first intermolecular example of olefin C–H activation by a second, different metal system of a precomplexed  $\pi$ -ethylene transition-metal complex and the concomitant formation of a novel alkene-bridged heterobimetallic Ir–Pt complex.

Reaction of  $(\text{H}_2\text{C=CH}_2)\text{Pt}(\text{PPh}_3)_2$  with 1 equiv of *trans*-Ir– $(\text{PPh}_3)_2(\text{CO})(\text{CF}_3\text{SO}_3)^-$  in  $\text{CH}_3\text{NO}_2$  at room temperature for 2 h gave  $[(\text{PPh}_3)_2(\text{CO})\text{Ir}(\mu\text{-H})(\mu\text{-}\eta^2\text{:}\eta^1\text{-CH=CH}_2)\text{Pt}(\text{PPh}_3)_2]^+\text{CF}_3\text{SO}_3^-$  (**1**) in 58% isolated yield (eq 1), as air-stable, bright-yellow crystals.<sup>6</sup> Compound **1** is very soluble in nitromethane, methylene chloride, and chloroform, but insoluble in hexane, benzene, and toluene. The structure of complex **1** was established

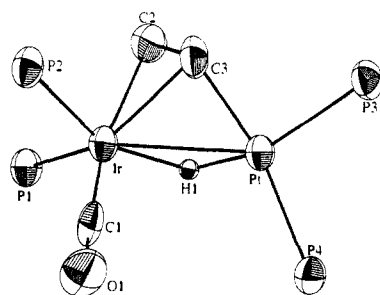
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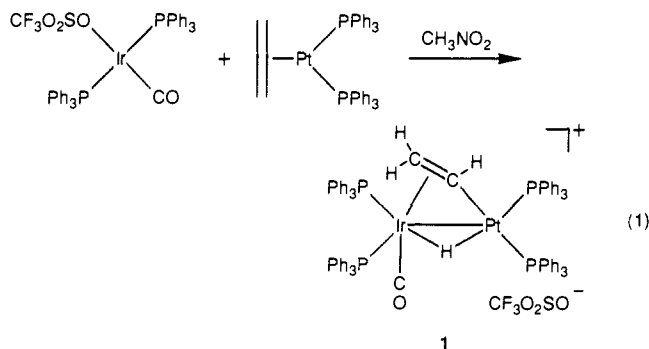
(5) While this work was in progress,  $\text{Ir}(\text{PPh}_3)_2(\text{CO})(\text{CF}_3\text{SO}_3)^-$  was published, i.e.: Liston, D. J.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1989**, *111*, 6643.

(6) Data on **1**: IR ( $\text{cm}^{-1}$ , KBr)  $\nu_{\text{CO}}$  1981 s;  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ) 7.45–7.10 (m, 12  $\text{C}_6\text{H}_5$ ), 5.60 (m,  $\mu\text{-CH}$ ), 2.32 (m,  $\mu\text{-CHH}'$ ), 1.35 (m,  $\mu\text{-CHH}''$ ), –11.54 (m,  $^1J_{\text{Pt-H}} = 515$  Hz, Ir–H–Pt);  $^{13}\text{C}\{^1\text{H}\}$  NMR (ppm,  $\text{CDCl}_3$ ) 176.3 (d,  $^2J_{\text{C-Pt}} = 12$  Hz, CO), 141.8 (dd,  $^2J_{\text{C-Pt}} = 85$ , 13 Hz,  $\mu\text{-CH}$ ), 135.6–127.8 (m, 12  $\text{C}_6\text{H}_5$ ), 121 (q,  $^1J_{\text{C-F}} = 321$  Hz,  $\text{CF}_3\text{SO}_3$ ), 37.6 (br s,  $\mu\text{-CH}_2$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR (ppm,  $\text{CDCl}_3$ ,  $\text{H}_3\text{PO}_4$ ) 21.3 (m,  $^1J_{\text{Pt-P}} = 2383$  Hz, P3 or P4), 13.6 (m,  $^1J_{\text{Pt-P}} = 4633$  Hz, P3 or P4), 9.4 (m,  $^2J_{\text{Pt-P}} < 90$  Hz, P1 or P2), 5.1 (m,  $^2J_{\text{Pt-P}} = 160$  Hz, P1 or P2);  $^{19}\text{F}$  NMR (ppm,  $\text{CDCl}_3$ ,  $\text{CFCl}_3$ ) –77.9 (s); mp (gradual darkening) 179–182 °C dec. Anal. Calcd for  $\text{C}_{76}\text{H}_{64}\text{F}_3\text{IrO}_4\text{P}_4\text{PtS}$ : C, 55.61; H, 3.93. Found: C, 55.35; H, 3.95.



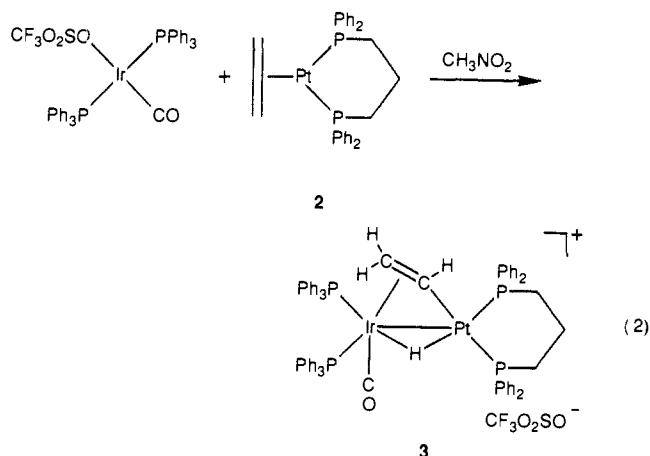
**Figure 1.** Simplified ORTEP representation of the cation of **1**. The phenyl rings of the PPh<sub>3</sub> groups and hydrogen atoms other than the  $\mu$ -hydride ligand are omitted for clarity.

by IR and NMR (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P, <sup>19</sup>F) spectroscopy and by satisfactory C and H elemental analysis.



The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **1** at ambient temperature displays four distinct multiplet resonances at 21.3, 13.6, 9.4, and 5.1 ppm, indicating inequivalent phosphorus environments and implying the presence of a metal-metal bond in **1**. The former two multiplets at 21.3 (<sup>1</sup>J<sub>Pt-P</sub> = 2383 Hz) and 13.6 (<sup>1</sup>J<sub>Pt-P</sub> = 4633 Hz) ppm with the large <sup>195</sup>Pt couplings are assigned to the two inequivalent triphenylphosphine groups (P3, P4) attached to the Pt metal center, while the latter two resonances at 9.4 (<sup>2</sup>J<sub>Pt-P</sub> < 90 Hz) and 5.1 (<sup>2</sup>J<sub>Pt-P</sub> = 160 Hz) ppm with small <sup>195</sup>Pt couplings are attributed to the remaining two triphenylphosphine ligands (P1, P2) bonded to the Ir atom. These observations demonstrate that the phosphorus nuclei are in mutual cis positions in both the Pt and Ir moieties. The <sup>1</sup>H NMR spectrum of **1** shows that the  $\mu$ -CH proton resonance is shifted downfield, appearing at  $\delta$  5.60 (m), compared to the  $\mu$ -CH<sub>2</sub> protons, which resonate at  $\delta$  2.32 (m) and  $\delta$  1.35 (m). The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum exhibits the  $\mu$ -CH carbon resonance downfield at 141.8 ppm (dd, <sup>2</sup>J<sub>C-P</sub> = 85, 13 Hz), while the  $\mu$ -CH<sub>2</sub> carbon appears upfield at 37.6 ppm (br s). These spectroscopic data support the formation of an  $\eta^2$ - $\eta^1$ -CH=CH<sub>2</sub> ligand in **1** and are consistent with those reported for the  $\eta^2$ -vinyl coordination mode.<sup>2c,k,7</sup> Furthermore, the <sup>1</sup>H NMR spectrum indicates the formation of a metal hydride complex, as evidenced by a diagnostic upfield complex multiplet centered at  $\delta$  -11.54 accompanied by the satellites due to <sup>195</sup>Pt coupling (<sup>1</sup>J<sub>Pt-H</sub> = 515 Hz). The characteristic <sup>1</sup>J<sub>Pt-H</sub> value<sup>8</sup> and the absence of both terminal Pt-H and Ir-H absorptions in the IR spectrum<sup>9</sup> suggest that an Ir-Pt bimetallic bridging hydride moiety is present. In addition, the IR spectrum of **1** shows  $\nu$ (CO) at 1981 (s) cm<sup>-1</sup> due to the terminal carbonyl stretch, indicating that the Ir-Pt bond is *not* supported by a CO bridge.

In analogy to the above reaction of the (H<sub>2</sub>C=CH<sub>2</sub>)Pt(PPh<sub>3</sub>)<sub>2</sub> complex, the interaction of cyclic analogue **2** with *trans*-Ir-(PPh<sub>3</sub>)<sub>2</sub>(CO)(CF<sub>3</sub>SO<sub>3</sub>) results in a 79% isolated yield of the related adduct **3** (eq 2). Likewise, preliminary results indicate that a similar reaction and alkyne C-H activation occurs in the reaction of *trans*-Ir(PPh<sub>3</sub>)<sub>2</sub>(CO)(CF<sub>3</sub>SO<sub>3</sub>) with the  $\pi$ -acetylene-Pt<sup>0</sup> complex (HC $\equiv$ CH)Pt(PPh<sub>3</sub>)<sub>2</sub>



A definitive structural assignment for **1** was established by X-ray crystallography. The bridging hydride ligand was located by difference Fourier methods. An ORTEP diagram of the cation is shown in Figure 1. The existence of a heterobimetallic Ir-Pt bond is indicated by the distance of 2.7484 (2) Å, which is shorter than the value of 2.8393 (12) Å found for the unbridged Ir-Ir distance in [( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)(CO)<sub>2</sub>Ir-Ir(CO)<sub>2</sub>( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)] [BF<sub>4</sub>]<sub>2</sub>.<sup>10</sup> The vinyl ligand is attached to the Pt atom by a  $\sigma$  bond through C3 and coordinated to the Ir center by  $\eta^2$  binding. The Pt-C3 distance is 2.014 (4) Å. The C2-C3 distance of 1.415 (6) Å is in between the bond distances of a C-C single and C=C double bond. The Ir-C2 and Ir-C3 distances are nearly equal at 2.197 (4) and 2.168 (4) Å, respectively. The bridging hydride is asymmetrically bound to the heterobimetallic center with a Pt-H1 distance of 1.4274 Å, an Ir-H1 distance of 1.6389 Å, and an Ir-H1-Pt angle of about 127°. The dihedral angle between the two planes defined by P1-Ir-P2 and P3-Pt-P4 is about 67°, thus relieving the steric repulsions between bulky ligands in the complex.

In summary, interaction of an Ir(I)-triflate complex with a  $\pi$ -ethylene-Pt<sup>0</sup> complex results in C-H activation and the ready formation of a novel heterobimetallic Ir-Pt complex. Although the oxidative addition of Hg-R or Fe-Cl bonds to (H<sub>2</sub>C=CH<sub>2</sub>)Pt(PPh<sub>3</sub>)<sub>2</sub> and the formation of heteronuclear Pt-M bonds, such as RHg-Pt(R)(PPh<sub>3</sub>)<sub>2</sub> and Cp(CO)<sub>2</sub>Fe-Pt(Cl)(PPh<sub>3</sub>)<sub>2</sub>, is well established,<sup>11</sup> as are hydrido-bridged Ir-Pt complexes,<sup>12</sup> the former reactions, without exception, involve loss of ethylene and the latter complexes do not contain bridging ligands other than hydrogen. Furthermore, the above system represents the first example of an intermolecular homogeneous transition-metal olefin C-H activation of a prior  $\pi$ -complexed alkene and the isolation of a unique ethylene-bridged Ir-Pt complex. The full scope of these reactions as well as the mechanism of formation and chemistry of these novel heterobimetallic systems are under investigation and will be reported in future papers.

**Acknowledgment.** We thank the NSF (CHE 8802622) for support of this research and Johnson-Matthey, Inc., for the generous loan of IrCl<sub>3</sub>·xH<sub>2</sub>O and K<sub>2</sub>PtCl<sub>4</sub>.

**Supplementary Material Available:** Experimental details of the X-ray diffraction study of complex **1**, including tables of crystallographic data, atomic positional and thermal parameters, and selected intramolecular distances and angles (18 pages); table of observed and calculated structure factors for complex **1** (37 pages). Ordering information is given on any current masthead page.

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