## **Alkyneselenolate vs Selenoketenyl Coordination:** Synthesis and Reactivity of $[Ir(SeC \equiv CC_6H_4Me-4)(CO)(PPh_3)_2]$

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Summary: The reaction of  $[IrCl(CO)(PPh_3)_2]$  with  $LiSeC \equiv CR$  ( $R = C_6H_4Me-4$ ) provides [ $Ir(SeC \equiv CR)(CO)$ - $(PPh_3)_2$  (1), which undergoes oxidative addition reactions with oxygen, methyl iodide, benzeneselenenyl chloride and bis(4-tolylethynyl)mercury to provide the complexes  $[Ir(SeC \equiv CR)(\eta^2 - O_2)(CO)(PPh_3)_2]$  (2),  $[Ir(CH_3) - O_2)(CO)(PPh_3)_2]$  $(Se\hat{C} \equiv CR)I(CO)(PPh_3)_2$  (3),  $[Ir(CH_3)I_2(CO)(PPh_3)_2]$  (4),  $[IrCl(SePh)(SeC \equiv CR)(CO)(PPh_3)_2]$  (5), and  $[Ir(C \equiv CR) (HgC \equiv CR)(SeC \equiv CR)(CO)(PPh_3)_2$  (6). The complexes 1-3, and 5, and 6 each contain the alkyneselenolate ligand bound to iridium in a monodentate manner through selenium.

## Introduction

We have recently reported the first examples of selenoketenyl ligands which result from the reaction of ketenyl complexes with Woollins' reagent (Scheme 1).<sup>2</sup> These results follow from our earlier studies on the related reactions of ketenyl complexes with Lawesson's thiating agent which provide analogous thioketenyl complexes.<sup>3</sup> Thioketenyl complexes had been previously reported by Mayr via the presumed coupling of thiocarbonyl and alkylidyne ligands on tungsten centers,<sup>4</sup> although we have recently had reason to reinterpret the mechanism of such processes.<sup>5</sup> Furthermore, Weiss has invoked thioketenyl intermediates in rationalizing the products of various coupling reactions of high-valent tungsten alkylidynes with alkyl isothiocyanates and related heterocumulenes.<sup>6</sup> In our studies of thio- and selenoketenyls of group 6 we have never encountered the decoupling of such a ligand into the notional alkylidyne and chalcocarbonyl constituents, even though such processes are often facile for ketenyls themselves, as is the reverse process whereby the majority of known ketenyl complexes have been prepared.<sup>7</sup> Given that





alkylidynes of the late transition metals are not apparently prone to coupling reactions with carbonyl coligands,<sup>8</sup> we reasoned that if ketenyl (or chalcoketenyl) ligands could be introduced into the coordination sphere of late transition metals, decoupling into alkylidyne and chalcocarbonyl ligands might actually be facile. Despite notable recent advances,<sup>9</sup> routes to late transition metal alkylidynes remain rare<sup>8</sup> providing impetus for developing new approaches to such complexes.

Weigand has reported that the reaction of [RuCl- $(PPh_3)_2(\eta - C_5H_5)$  with LiSC=CR (R = CMe<sub>3</sub>, cyclohexyl, Ph) provides the alkynethiolato complexes [Ru( $\sigma$ -SC= CR)(PPh<sub>3</sub>)<sub>2</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)], wherein the organosulfur ligand is bound only through sulfur as a conventional thiolate (A, Chart 1).<sup>10</sup> One phosphine ligand in [Ru( $\sigma$ -SC= CPh)( $PPh_3$ )<sub>2</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] is clearly labile, as indicated by its replacement with carbon monoxide; however the presumed 16 electron intermediate does not appear to rearrange to a thicketenyl ligand (B, Chart 1).

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Chart 1. Coordination Modes for Alkynyl Chalcogenolates and Alkynyl Chalcoethers



In pursuit of alternative routes to selenoketenyl complexes we have investigated the reactions of Vaska's complex [IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] with LiSeC=CC<sub>6</sub>H<sub>4</sub>Me-4, the results of which are reported herein.

## **Experimental Section**

General Comments. All manipulations were carried out under anaerobic conditions using conventional Schlenk and vacuum line techniques. Solvents as received from commercial sources were distilled from a suitable drying agent and purged with nitrogen prior to use. Vaska's complex was prepared according to a published procedure,<sup>11</sup> with the exception that hexachloroiridic acid was used in place of iridium(III) chloride with no substantial compromise in yield. All other reagents were used as received from commercial sources.  ${}^{1}H$ .  ${}^{13}C{}^{1}H$ . and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded with a JEOL JNM EX270 NMR spectrometer and calibrated against internal SiMe<sub>4</sub> (<sup>1</sup>H), internal CDCl<sub>3</sub> (<sup>13</sup>C) or external H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P) references. "tv" indicates a virtual triplet arising from the trans-bis(phosphine) arrangement, with "apparent" couplings given. Infrared spectra were recorded both as dichloromethane solutions, and Nujol mulls, using Perkin-Elmer 1720-X or Mattson Series 1 FT-IR spectrometers. Characteristic "fingerprint" bands for PPh3 are omitted. FAB-mass spectrometry was carried out using an Autospec Q instrument with 3-nitrobenzyl alcohol as a matrix. Compositional assignments are based on simulation of isotopic distributions. Elemental analysis was carried out by the University of North London Microanalytical Service.

Preparation of  $[Ir(SeC \equiv CC_6H_4Me-4)(CO)(PPh_3)_2]$  (1). A solution of 4-ethynyltoluene (0.037 g, 0.32 mmol) in diethyl ether (10 mL) was cooled to -20 °C and then treated with <sup>*n*</sup>BuLi (0.16 mL, 2.0 mol  $L^{-3}$ , 0.32 mmol) and the mixture stirred for 20 min. The solution was allowed to warm to room temperature, and then gray selenium (0.030 g) was added and the mixture stirred for a further 30 min or until all the selenium had dissolved. The resulting (air-sensitive) solution was transferred by cannula to a flask containing [IrCl(CO)-(PPh<sub>3</sub>)<sub>2</sub>] (0.25 g, 0.32 mmol) in tetrahydrofuran (25 mL). The mixture was stirred for 15 min (darkens somewhat) and then transferred by filter cannula to a second Schlenk tube. The total solvent volume was reduced in vacuo to ca. 5 mL and then diluted with diethyl ether (20 mL) resulting in the precipitation of a bright yellow solid which was recrystallized from a mixture of dichloromethane and diethyl ether. Yield: 0.20 g (67%). IR: CH<sub>2</sub>Cl<sub>2</sub>, 1957 [v(CO)] cm<sup>-1</sup>; Nujol, 2142 [v- $(C \equiv C)$ ], 1959 [ $\nu(CO)$ ], 817 [ $\delta(C_6H_4)$ ] cm<sup>-1</sup>. NMR (CDCl<sub>3</sub>, 25 °C): <sup>1</sup>H,  $\delta$  2.18 [s, 3 H, CH<sub>3</sub>], 6.04, 6.69 [(AB)<sub>2</sub>, 4 H, C<sub>6</sub>H<sub>4</sub>,  $J(H_AH_B) = 7.92$  Hz], 7.34–7.88 [m, 30 H, C<sub>6</sub>H<sub>5</sub>] ppm; <sup>13</sup>C{<sup>1</sup>H}, 175.8 [t, IrCO, J(PC) = 25.0], 135.0 [t<sup>v</sup>, C<sup>2.6</sup>(C<sub>6</sub>H<sub>5</sub>), J(PC) = 6.3], 131.2 [t<sup>v</sup>, C<sup>1</sup>(C<sub>6</sub>H<sub>5</sub>), J(PC) = 19.7 Hz], 130.3 [s, C<sup>4</sup>(C<sub>6</sub>H<sub>5</sub>)], 127.8 [t<sup>v</sup>, C<sup>3.5</sup>(C<sub>6</sub>H<sub>5</sub>), J(PC) not resolved], 122.4 [C<sup>4</sup>(C<sub>6</sub>H<sub>4</sub>)] (remaining C<sub>6</sub>H<sub>4</sub> resonances obscured by those for C<sub>6</sub>H<sub>5</sub> groups), 94.9 [CC $\equiv$ ], 68.0 [Se $C \equiv$ ], 21.3 [CH<sub>3</sub>] ppm; <sup>31</sup>P{<sup>1</sup>H},  $\delta$  27.9 ppm. FAB-MS: m/z = 940 [M]<sup>+</sup>, 712 [M – CO]<sup>+</sup>, 796 [M – CO – CCR]<sup>+</sup>, 745 [Ir(CO)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, 715 [Ir(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, 453 [IrPPh<sub>3</sub>]<sup>+</sup>, 263 [HPPh<sub>3</sub>]<sup>+</sup>. Anal. Found: C, 59.0; H, 4.0. Calcd for C<sub>46</sub>H<sub>37</sub>IrOP<sub>2</sub>Se: C, 58.8; H, 4.0.

Preparation of  $[Ir(SeC \equiv CR)(\eta^2 \cdot O_2)(CO)(PPh_3)_2]$  (2). A solution of [Ir(SeC≡CR)(CO)(PPh<sub>3</sub>)<sub>2</sub>] (1) (0.100 g, 0.11 mmol) in dichloromethane (20 mL) was stirred under air for 12 h (quantitative conversion by FT-IR). The solvent was removed under reduced pressure and the residue crystallized by addition of diethyl ether. Yield: 0.055 g (54%). IR: CH<sub>2</sub>Cl<sub>2</sub>, 2035  $[\nu(CO)]$  cm<sup>-1</sup>; Nujol, 2132  $[\nu(C=C)]$ , 1982  $[\nu(CO)]$ , 852  $[\nu(IrO_2)]$ , 815 [δ(C<sub>6</sub>H<sub>4</sub>)] cm<sup>-1</sup>. NMR (CDCl<sub>3</sub>, 25 °C): <sup>1</sup>H, δ 2.29 [s, 3 H,  $CH_3$ ], 6.96, 7.03 [(AB)<sub>2</sub>, 4 H, C<sub>6</sub>H<sub>4</sub>,  $J(H_AH_B) = 7.92$  Hz], 7.30-7.93 [m, 30 H, C<sub>6</sub>H<sub>5</sub>] ppm;  ${}^{13}C{}^{1}H$ , 168.8 [t, IrCO, J(PC) = 9.5], 134.7 [t<sup>v</sup>,  $C^{2,6}(C_6H_5)$ , J(PC) = 5.3], 132.2 [t<sup>v</sup>,  $C^1(C_6H_5)$ ], 131.0 [s,  $C^4(C_6H_5)$ ], 128.2 [t<sup>v</sup>,  $C^{3,5}(C_6H_5)$ , J(PC) 4.5 Hz], 122.7  $[C^4(C_6H_4)]$  (remaining  $C_6H_4$  resonances obscured by those for C<sub>6</sub>H<sub>5</sub> groups), 89.4 [C*C*≡], 75.7 [Se*C*≡], 21.5 [CH<sub>3</sub>] ppm; <sup>31</sup>P-{<sup>1</sup>H},  $\delta$  5.6 ppm. FAB-MS:  $m/z = 971 \text{ [M]}^+$ , 940 [M - O<sub>2</sub>]<sup>+</sup>, 712  $[M - O_2 - CO]^+$ , 796  $[M - CO - O_2 - CCR]^+$ , 745 [Ir- $(CO)(PPh_3)_2]^+$ , 715  $[Ir(PPh_3)_2]^+$ , 453  $[IrPPh_3]$ , 263  $[HPPh_3]^+$ . Anal. Found: C, 56.5; H, 3.9. Calcd for C<sub>46</sub>H<sub>37</sub>IrO<sub>3</sub>P<sub>2</sub>Se: C, 56.9: H. 3.8.

**Preparation of [Ir(CH<sub>3</sub>)(SeC=CR)I(CO)(PPh<sub>3</sub>)<sub>2</sub>] (3)** and [Ir(CH<sub>3</sub>)I<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>] (4). [Ir(SeC=CR)(CO)(PPh<sub>3</sub>)<sub>2</sub>] (1) (0.100 g, 0.11 mmol) was stirred in iodomethane (3 mL) for 16 h. Diethyl ether (15 mL) was added and the resulting precipitate filtered off to provide pale yellow microcrystals of **3.** Yield: 0.035 g (30%). The filtrate was diluted with ethanol (20 mL) and the solvent volume reduced slowly to afford fibrous crystals of **4.** Yield: 0.070 g (69%). The complex could be recrystallized from a mixture of dichloromethane and ethanol as a CH<sub>2</sub>Cl<sub>2</sub> hemisolvate.

(a) Data for (3). IR (Nujol): 2134 [ $\nu$ (C=C)], 2049 [ $\nu$ (CO)] cm<sup>-1</sup>. NMR (CDCl<sub>3</sub>, 25 °C): <sup>1</sup>H,  $\delta$  0.66 [t, 3 H, IrCH<sub>3</sub>, *J*(PH) = 5.1], 2.33 [s, 3 H, C-CH<sub>3</sub>], 7.03, 7.19 [(AB)<sub>2</sub>, 4 H, C<sub>6</sub>H<sub>4</sub>, *J*(H<sub>A</sub>H<sub>B</sub>) = 7.92 Hz], 7.32, 7.89 [m × 2, 30 H, C<sub>6</sub>H<sub>5</sub>] ppm; <sup>31</sup>P-{<sup>1</sup>H},  $\delta$  -21.1 ppm. FAB-MS: *m*/*z* =1078 [M]<sup>+</sup>, 887 [M - SeCCR]<sup>+</sup>. Anal. Found: C, 50.5; H, 4.0. Calcd for C<sub>47</sub>H<sub>40</sub>-IIrOP<sub>2</sub>Se•0.5CH<sub>2</sub>Cl<sub>2</sub>: C, 50.7; H, 3.7.

(b) Data for 4. IR (CH<sub>2</sub>Cl<sub>2</sub>): 2044 [ $\nu$ (CO)] cm<sup>-1</sup>. IR (Nujol): 2028 [ $\nu$ (CO)], 1241 [ $\nu$ (IrCH<sub>3</sub>)] cm<sup>-1</sup>. NMR (CDCl<sub>3</sub>, 25 °C): <sup>1</sup>H,  $\delta$  1.14 [t, 3 H, IrCH<sub>3</sub>, J(PH) = 5.2 Hz], 7.19–8.01 [m, 30 H, C<sub>6</sub>H<sub>5</sub>] ppm; <sup>31</sup>P{<sup>1</sup>H},  $\delta$  –25.4 ppm. FAB-MS: m/z = 1015 [HM]<sup>+</sup>, 887 [M – I]<sup>+</sup>, 859 [M – I – CO]<sup>+</sup>. Anal. Found: C, 44.9; H, 3.3. Calcd for C<sub>38</sub>H<sub>33</sub>I<sub>2</sub>IrOP<sub>2</sub>: C, 45.0; H, 3.3.

Preparation of [IrCl(SePh)(SeC=CR)(CO)(PPh<sub>3</sub>)<sub>2</sub>] (5). A solution of  $[Ir(SeC \equiv CR)(CO)(PPh_3)_2]$  (1) (0.10 g, 0.11 mmol) in tetrahydrofuran (15 mL) was treated with benzeneselenenyl chloride (0.022 g, 0.11 mmol) and the mixture stirred for 15 min. The solvent volume was reduced in vacuo to ca. 10 mL and then diluted with diethyl ether (15 mL) to provide an orange solid which was recrystallized from a mixture of dichloromethane and diethyl ether. Yield: 0.098 g (75%). IR  $(CH_2Cl_2)$ : 2134 [ $\nu$ (C=C)], 2059 [ $\nu$ (CO)] cm<sup>-1</sup>. IR (Nujol): 2130  $[\nu(C=C)]$ , 2049  $[\nu(CO)]$ , 815  $[\delta(C_6H_4)]$  cm<sup>-1</sup>. NMR (CDCl<sub>3</sub>, 25 °C): <sup>1</sup>H,  $\delta$  2.15 [s, 3 H, CH<sub>3</sub>], 6.49, 6.68 [(AB)<sub>2</sub>, 4 H, C<sub>6</sub>H<sub>4</sub>,  $J(H_AH_B) = 7.92 \text{ Hz}$ ], 6.8–8.2 [m, 35 H, C<sub>6</sub>H<sub>5</sub>] ppm; <sup>31</sup>P{<sup>1</sup>H},  $\delta$ -26.4 ppm. FAB-MS: m/z = 1130 [M]<sup>+</sup>, 1094 [M - Cl]<sup>+</sup>, 1066 [M - Cl - CO]<sup>+</sup>, 1017 [M - CCR]<sup>+</sup>, 937 [M - SePh]<sup>+</sup>, 937 [M - Cl - SePh]<sup>+</sup>, 910 [M - Cl - CO - SePh]<sup>+</sup>. Anal. Found: C, 51.4; H, 3.8. Calcd for C<sub>52</sub>H<sub>42</sub>ClIrOP<sub>2</sub>Se<sub>2</sub>·1.5CH<sub>2</sub>Cl<sub>2</sub>: C, 51.1; H, 3.6.

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Preparation of [Ir(C=CR)(HgC=CR)(SeC=CR)(CO)- $(PPh_3)_2$  (6). A solution of  $[Ir(SeC \equiv CR)(CO)(PPh_3)_2]$  (1) (0.10 g, 0.11 mmol) in tetrahydrofuran (15 mL) was treated with solid bis(4-tolylethynyl)mercury(II) (0.046 g, 0.11 mmol) and the mixture stirred for 1 h. The solvent volume was reduced in vacuo to ca. 5 mL and then diluted with diethyl ether (20 mL) to provide a yellow solid which was recrystallized from a mixture of dichloromethane and diethyl ether. Yield: 0.055 g (36%). IR (thf): 2130 [ $\nu$ (C=C)], 2042 [ $\nu$ (CO)] cm<sup>-1</sup>. IR (Nujol): 2125 [ $\nu$ (C=C)], 2034 [ $\nu$ (CO)], 815 [ $\delta$ (C<sub>6</sub>H<sub>4</sub>)] cm<sup>-1</sup>. NMR (CDCl<sub>3</sub>, 25 °C): <sup>1</sup>H,  $\delta$  2.28, 2.30, 2.31 [s  $\times$  3, 3 H  $\times$  3,  $CH_3 \times 3$ ], 6.8–7.2 [(AB)<sub>2</sub> × 3, 12 H, C<sub>6</sub>H<sub>4</sub> × 3], 7.34, 8.08 [m × 2, 30 H, C<sub>6</sub>H<sub>5</sub>] ppm; <sup>13</sup>C{<sup>1</sup>H}, 173.8 [t, IrCO, J(PC) = 6.5 ], 146.4, 137.5, 135.5 [C<sup>4</sup>(C<sub>6</sub>H<sub>4</sub>)  $\times$  3], 134.5 [t<sup>v</sup>, C<sup>1</sup>(C<sub>6</sub>H<sub>5</sub>), J(PC) = 21.9], 133.9 [t<sup>v</sup>,  $C^{2,6}(C_6H_5)$ , J(PC) = 4.9], 131.9, 131.5, 130.3, 128.9, 128.8 [C<sup>2,3,5,6</sup>(C<sub>6</sub>H<sub>4</sub>)], 130.6 [C<sup>4</sup>(C<sub>6</sub>H<sub>5</sub>)], 128.4 [t<sup>v</sup>, C<sup>3,5</sup>(C<sub>6</sub>H<sub>5</sub>), J(PC) = 5.4], 125.0, 123.2, 120.8 [C<sup>1</sup>(C<sub>6</sub>H<sub>4</sub>) × 3], 115.7 [IrC=C], 101.4 [HgC=C], 86.8 [SeC=C], 80.6 [t, IrC=, J(PC) = 17.2 Hz], 79.4 [HgC≡], 68.1 [SeC≡], 21.6, 21.5, 21.4 [CH<sub>3</sub> × 3] ppm; <sup>31</sup>P- $\{^{1}H\}, \delta - 18.6 [J(PSe) = 27.8, J(PHg) = 233.7 Hz] ppm. FAB-$ MS:  $m/z = 1252 [M - CCR]^+$ , 1175  $[M - SeCCR]^+$ , 1055 [M- HgCCR]<sup>+</sup>, 975 [M - Hg - SeCCR]<sup>+</sup>, 947 [M - Hg - SeCCR - CO]<sup>+</sup>, 860 [M - HgCCR - SeCCR]<sup>+</sup>, 831 [M - HgCCR - $SeCCR - CO]^+$ , 745  $[Ir(CO)(PPh_3)_2]^+$ , 715  $[Ir(PPh_3)_2]^+$ , 559 [IrPPh<sub>3</sub>]<sup>+</sup>. Anal. Found: C, 56.2; H, 3.9. Calcd for C<sub>64</sub>H<sub>51</sub>-HgIrOP<sub>2</sub>Se: 56.1; H, 3.8.

## **Results and Discussion**

A solution of LiSeC=CC<sub>6</sub>H<sub>4</sub>Me-4 was prepared by first deprotonating 4-ethynyl toluene with <sup>*n*</sup>BuLi, followed by treatment with elemental selenium<sup>12</sup> (Scheme 2). Treating a tetrahydrofuran solution of [IrCl(CO)-(PPh<sub>3</sub>)<sub>2</sub>] with this solution leads to the formation of a bright yellow solution from which the complex [Ir(SeC= CR)(CO)(PPh<sub>3</sub>)<sub>2</sub>] (1) (hereafter R = C<sub>6</sub>H<sub>4</sub>Me-4) may be isolated in 66% yield. Solutions of complex 1 must be manipulated under total exclusion of air due to facile formation of the dioxygen adduct [Ir(SeC=CR)( $\eta^2$ -O<sub>2</sub>)-(CO)(PPh<sub>3</sub>)<sub>2</sub>] (vide infra); however, it is indefinitely stable in the absence of air and may be handled briefly in air as a solid.

The gross formulation of 1 follows from elemental microanalytical data and FAB-mass spectrometry. The latter includes an isotopic distribution attributable to the molecular ion in addition to fragmentations due to loss of the alkyneselenolate and/or carbonyl ligands. The infrared spectrum reveals absorptions assignable to the carbonyl ligand (Nujol: 1959 cm<sup>-1</sup>) and the free alkynyl group  $[\nu(C \equiv C) = 2142, \delta(C_6H_4) = 817 \text{ cm}^{-1}]$ . No band could be identified due to  $\nu$ (C–Se); however, these are typically weak and buried within the phosphine fingerprint. The <sup>1</sup>H NMR spectrum of **1** is unremarkable; however, the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum is more informative. The appearance of a triplet resonance for the carbonyl ligand [175.8 ppm, J(PC) = 25.0 Hz] confirms the trans-bis(phosphine) stereochemistry at iridium, and this is further supported by a singlet  ${}^{31}P{}^{1}H$  NMR resonance being observed at 27.9 ppm. The alkynyl group gives rise to two resonances at 94.9 and 68.0 ppm. These compare well with those reported for  $PhSeC \equiv$ CR (103.2, 68.2 ppm).<sup>13</sup> These data taken together indicate that the organoselenium ligand adopts the  $\eta^{1}$ -

Scheme 2. Synthesis and Reactions of  $[Ir(SeC \equiv CR)(CO)(PPh_3)_2]$  (R = C<sub>6</sub>H<sub>4</sub>Me-4, L = PPh<sub>3</sub>)



Se mode of coordination, previously established for alkynethiolates<sup>10</sup> but which is novel for selenium. It is noteworthy that this is despite the alternative  $\eta^2$ -C,C mode offering the possibility of providing 3 valence electrons to iridium and is clearly a feature of the favorable and ubiquitous 16-electron d<sup>8</sup>-ML<sub>4</sub> square planar geometry.

The selenolate clearly serves as a potent donor, as indicated by the significant increase in the propensity of 1 to coordinate dioxygen irreversibly cf Vaska's complex. Thus, the orange dioxygen adduct forms rapidly in solution at room temperature. Spectroscopic data for  $[Ir(\sigma-SeC \equiv CR)(\eta^2-O_2)(CO)(PPh_3)_2]$  (2) are directly comparable to those of the precursor, with the exception that an infrared absorption attributable to the  $IrO_2$  group is noted at 857 cm<sup>-1</sup>. This oxidation of the iridium center is accompanied by an increase in  $\nu$ (CO) to 1982 cm<sup>-1</sup> and a shift in the value of  $\delta$ (<sup>31</sup>P) to 5.7 ppm. The effect of halide replacement upon the facility and reversibility of dioxygen binding in the complexes [IrX(CO)(PPh<sub>3</sub>)<sub>2</sub>] has long been established by Roper,<sup>14</sup> and the present result is entirely consistent with the established trends.

**Further Oxidative Addition Reactions.** The oxidative addition of methyl iodide to Vaska's complex provides  $[IrCl(CH_3)I(CO)(PPh_3)_2]^{15}$  and is a sufficiently fundamental process that it features in most organo-

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metallic textbooks. The reaction of 1 with methyl iodide proceeds initially in a completely analogous manner to provide  $[Ir(CH_3)I(SeC \equiv CR)(CO)(PPh_3)_2]$  (3); however, with longer reaction times and excess CH<sub>3</sub>I the ultimate product is  $[Ir(CH_3)I_2(CO)(PPh_3)_2]$  (4) and presumably MeSeC=CR, although this was not identified. The complex 4 has been described previously as resulting from an alternative route.<sup>16</sup> Thus, secondary alkylation of the alkyneselenolate appears to be followed by dissociation of the alkynyl selenoether and replacement by iodide. Complexes of alkynyl selenoethers remain rare,<sup>2,17,18</sup> although Angelici's elegant studies on the synthetic versatility of alkynyl thioether complexes<sup>19</sup> presages a similarly rich chemistry for selenium. The apparent lability of the MeSeC≡CR group is consistent with the generally accepted weak coordination of selenoethers. It should thus be emphasized that the known complexes of alkynyl selenoethers involve either  $\eta^2$ -*C*.*C* coordination through the alkyne group ( $\mathbf{C}$ , Chart 1)<sup>2,17</sup> or are of the dicobaltaterahedrane form (**D**, Chart 1),<sup>18</sup> again involving coordination through the alkynyl group rather than the selenoether. We have previously shown that the alkylation of  $[M(\eta^2-SeCCR)(CO)(PPh_3)]{HB}$  $(pz)_{3}$  (M = Mo, W; pz = pyrazol-1-yl) with methyl iodide provides  $[M(\eta^2-MeSeC \equiv CR)(CO)(PPh_3){HB-$ (pz)<sub>3</sub>]I.<sup>2</sup> Hence, perhaps unsurprisingly, the process of alkylation is dependent upon the mode of coordination of the "SeCCR" ligand and the metal center involved.

The oxidative addition of benzeneselenenyl chloride to **1** takes a more conventional route to provide [IrCl-(SePh)(SeC $\equiv$ CR)(CO)(PPh<sub>3</sub>)<sub>2</sub>] (**5**), a complex with two different selenolate ligands. Although only one isomer is formed (<sup>31</sup>P NMR), the stereochemistry at iridium does not follow unambiguously from spectroscopic data. It is however reasonable to assume that a two-step process occurs to deliver the two components to opposite faces of the substrate providing the stereochemistry shown in Scheme 2.

Finally, the reaction of **1** with bis(4-tolylethynyl)mercury was investigated. Our motives for such an investigation were purely aesthetic, as the desired

complex would provide the unusual situation wherein alkynyl groups were bound to three different elements, viz.  $[Ir(C \equiv CR)(HgC \equiv CR)(SeC \equiv CR)(CO)(PPh_3)_2]$  (6). This anticipation follows from Collman's synthesis of [Ir- $(C \equiv CPh)Cl(HgC \equiv CR)(CO)(PPh_3)_2$  from Vaska's complex and bis(phenylethynyl)mercury<sup>20</sup> and our own observation that such processes are involved in the catalytic demercuration of bis(alkynyl)mercurials by the analogous rhodium complex [RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub>].<sup>21</sup> The spectroscopic data clearly identify the nature of 6: Although no molecular ion is observed, the FAB mass spectrum features a substantial peak due to loss of one alkynyl group in addition to further fragmentations involving loss of "SeCCR" and (less abundantly) "HgC-CR" groups. Notably no peak is observed due to the sole loss of mercury, although in solution such a process is facile for  $[Ir(C \equiv CPh)Cl(HgC \equiv CR)(CO)(PPh_3)_2]$ . The comparatively high value of  $\nu$ (CO) (thf: 2042 cm<sup>-1</sup>) suggests that this ligand is trans to the ligand with the lowest Lewis basicity toward the metal, i.e., the alkynyl group. Infrared spectroscopy fails to adequately resolve the three  $\nu$ (C=C) absorptions occurring around 2130 cm<sup>-1</sup>; however, three distinct alkynyl environments are evident in the <sup>1</sup>H and <sup>13</sup>C NMR spectra. The <sup>31</sup>P NMR spectrum consists of a singlet resonance ( $\delta$  –18.6 ppm) showing satellite resonances arising from coupling to selenium [J(SeP) = 27.8 Hz] and mercury [J(HgP) =233.7 Hz], further confirming the proposed stereochemistry.

In conclusion, the preliminary results discussed above show that (i) alkyneselenolate ligands may be introduced by simple metal halide metathesis, (ii) the coordination mode of the "SeCCR" fragment is dependent on the metal center involved, (iii) the alkynyl selenolate ligand can support simple oxidative addition reactions on iridium(I) allowing the preparation of mixed bis(selenolate) complexes, and (iv) the coordination mode of the "SeCCR" group affects the outcome of alkylation reactions.

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