

Formal Vinylidene Ligand Insertion into a Metal Halide Bond

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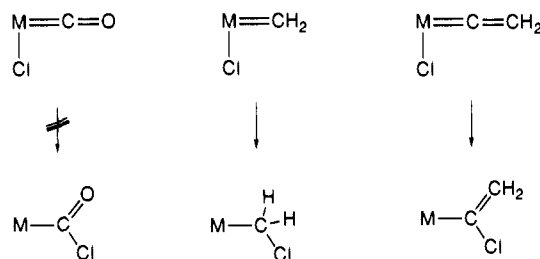
Received April 14, 1995

Migratory insertion represents an important reaction pathway for transition metal complexes of π -acceptor ligands such as carbon monoxide,¹ carbene,² and vinylidene.³ In the case of $Mn(R)(CO)_5$, Berke and Hoffmann have calculated that the activation energy for migration of R to carbon monoxide increases from ~ 20 to 66 kcal mol⁻¹ on going from R = CH₃ to R = Cl.⁴ In general, migratory insertions involving carbene ligands are more facile than for carbon monoxide,^{4,5} and halide migration to a carbene ligand may indeed be involved in the reactions of diazo compounds with transition metal halides (Chart 1).⁶ The migration of halide from the α -chlorovinyl ligand to a transition metal has previously been observed.⁷ Herein, we report the first examples of formal vinylidene ligand insertion into metal halide bonds to generate α -halovinyl ligands.

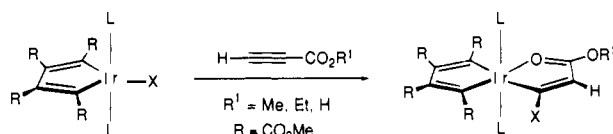
The metal-mediated conversion of terminal alkynes to vinylidene ligands is attracting considerable attention due to the wide scope of the reaction and the fascinating properties and reactivity exhibited by this ligand class.⁸ We previously reported the reactions of $Ir(CR=CR=CR)(PPh_3)_2Cl$ (**1-Cl**, R = CO₂CH₃)⁹ with 3-butyne-1-ol to give the metallacycle-carbene complex **2**,¹⁰ and **1-Cl** with propargyl alcohol to give the ethenyl complex **3**¹¹ (Scheme 1). Both reactions appear to proceed via vinylidene intermediates.

We have now found that, in methylene chloride at 25 °C (12 h), methyl propiolate (0.034 M) and **1-Cl** (0.031 M) are

Chart 1



converted to oxametallacycle **4-Cl**, which is isolated as a faint yellow powder in 93% yield (eq 1).^{12,13} The observation of five methyl singlets and a one-hydrogen singlet at δ 6.04 (1H) in the ¹H NMR spectrum (CDCl₃) of **4-Cl** supports the presence of a methyl propiolate-derived ligand. In the ¹³C{¹H} NMR spectrum (CD₂Cl₂), a downfield resonance is observed at 209 (t, J = 8.4 Hz) ppm, consistent with a new carbon-bound ligand coupled to two equivalent phosphorus atoms, but inconsistent with either η^2 -alkyne or vinylidene ligands.



- 1-Cl**, X = Cl, L = PPh₃
1-Br, X = Br, L = PPh₃
1-I, X = I, L = PPh₃
8, X = Cl, L = AsPh₃

- 4-Cl**, X = Cl, L = PPh₃, R¹ = Me
4-Br, X = Cl, L = PPh₃, R¹ = Me
5, X = Cl, L = PPh₃, R¹ = Et
6, X = Cl, L = PPh₃, R¹ = H
7, X = Cl, L = AsPh₃, R¹ = Me

Ethyl propiolate and propynoic acid also undergo reaction with **1-Cl** to give **5** (83%) and **6** (77%), respectively, both of which exhibit spectroscopic properties similar to those observed for **4-Cl**.¹³ Ultimately, the structures of **4-Cl**, **5**, and **6** were assigned by comparison of spectroscopic properties to those of the triphenylarsine complex **7**, which was formed from **8** and methyl propiolate, and characterized by a single-crystal X-ray diffraction study (Figure 1).¹⁴ Complex **7** exhibits large deviations from ideal octahedral geometry, with the C(13)–Ir–O(9) and C(1)–Ir–C(4) angles constrained by the metal-

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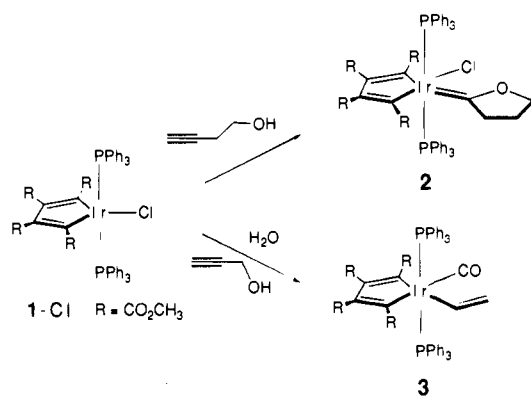
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(12) Data for **4-Cl**: mp 177–178 °C; IR (Nujol) 1720 cm⁻¹ (vs), 1700 (s), 1680 (vs), 1575 (vs), 1540 (w), 1260 (s), 1200 (vs); ¹H NMR (CDCl₃, 300 MHz): δ 7.6–7.4 (m), 7.25–7.10 (m), 6.04 (s, 1H), 3.63 (s, 3H), 3.53 (s, 3H), 3.45 (s, 3H), 3.33 (s, 3H), 3.31 (s, 3H); ¹³C {¹H} NMR (CDCl₃, 75.57 MHz) δ 209.4 (t, J = 8.4 Hz, IrC(Cl)=), 183.6, 175.7, 173.2, 168.3, 164.9, 153.3 (t, J = 9.4 Hz), 152.4, 146.5, (t, J = 7.4 Hz), 146.1, 135.4 (t, J = 5.2 Hz), 130.1, 130.0 (t, J = 27.2 Hz), 127.4 (t, J = 5.0 Hz), 126.4, 50.85, 50.76, 50.5. Anal. Calcd for: C₅₂H₄₆ClIrP₂O₁₀: C, 55.75; H, 4.14. Found: C, 55.44; H, 4.03.

(13) See supporting information for full characterization.

Scheme 1



lacycle rings to 75.4(7)° and 78.6(8)°, respectively. The 1.741-(23) Å C(13)–Cl distance compares with a C–Cl distance of 1.809(6) Å in *trans*-Pt(CCl=CH₂)₂(PMe₂Ph)₂¹⁵ and a 1.728(7) Å distance in vinyl chloride.¹⁶

The iridium bromide metallacycle **1-Br** also undergoes reaction with methyl propiolate to give oxametallacycle **4-Br**, whereas the iridium iodide complex **1-I** fails to react with methyl propiolate over the course of 1 week at room temperature. The observed pseudo-first-order rate constants for disappearance of **1-Cl** (0.012 M) and **1-Br** (0.012 M) in benzene-*d*₆ (0.19 M methyl propiolate) were found to be 5.0 × 10⁻⁴ s⁻¹ and 5.9 × 10⁻⁵ s⁻¹, respectively. In the presence of added halide (0.013 M PPNCI), the observed pseudo-first-order rate constant for disappearance of **1-Cl** (0.012 M, with 0.24 M methyl propiolate) in benzene-*d*₆ was determined to be 6.0 × 10⁻⁴ s⁻¹. The observation that **4-Cl** and ethyl propiolate fail to give **5** at room temperature indicates that **4-Cl** does not revert to free alkyne and **1-Cl** under the reaction conditions.

The formation of **4-Cl** from **1-Cl** and methyl propiolate is most readily explained by generation of a vinylidene intermediate. The migration process may involve halide attack on a cationic vinylidene intermediate (**I**)¹⁵ or an intramolecular migration of halide from the metal to the vinylidene ligand (**II**, Chart 2). The kinetic results do not allow a distinction to be made between these two processes. Rapid exchange of halide

between Ir(CR=CRCR=CR)(PPh₃)₂Cl (**1-Cl-*d***₁₂, R = CO₂CD₃) and **1-Br** in benzene-*d*₆ precludes the use of a crossover experiment to resolve this issue.

The results reported herein stand in interesting contrast to Werner's synthesis of [*trans*-Rh(=C=CHCO₂Et)(PⁱPr₃)₂Cl], a complex for which halide migration has not been observed.¹⁷ Product stabilization by oxygen chelation is no doubt a key feature of the halide migration. To date we have failed to

(14) Crystal data for **7**: C₅₂H₄₆As₂ClIrO₁₀, monoclinic, *P*₂₁/*n*, *a* = 10.768(3) Å, *b* = 21.470(5) Å, *c* = 21.987(7) Å, *V* = 5035(2) Å³, *Z* = 4, *D*_{calcd} = 1.594 g cm⁻³, μ(Mo Kα) = 40.65 cm⁻¹, *T* = 233 K. Of 9379 absorption-corrected data collected (2θ_{max} = 50°, Siemens P4 diffractometer), 8862 were independent, and 4390 were observed (5σ_{F_o} cutoff). All non-hydrogen atoms, except for the carbon atoms contained in the phenyl rings, were refined with anisotropic thermal parameters. *R*_F = 7.23%, and *R*_{wF} = 9.66%.

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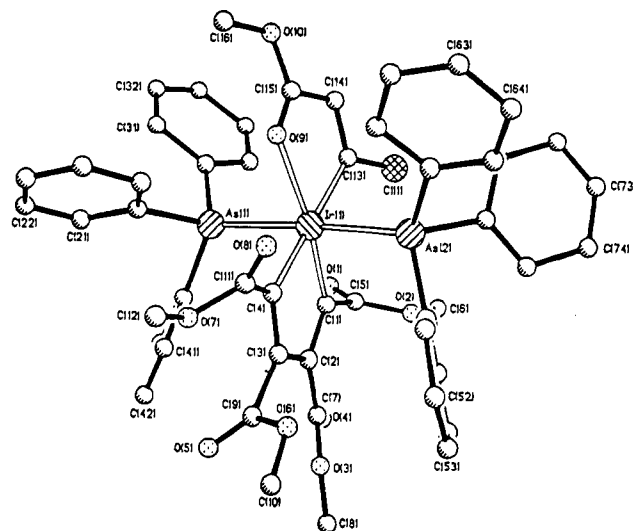
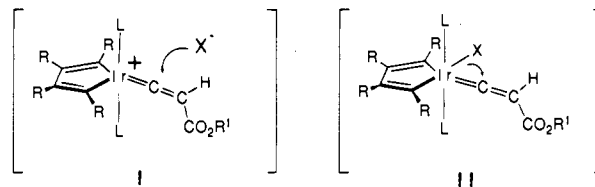


Figure 1. ORTEP drawing of **7** showing selected atom labeling. Distances (Å) and angles (deg): Ir–O(9) 2.199(14), Ir–C(1) 1.992(19), Ir–C(4) 2.087(24), Ir–C(13) 2.103(24), O(1)–C(5) 1.202(27), O(2)–C(5) 1.312(28), O(9)–C(15) 1.266(30), C(1)–C(2) 1.357(29), C(1)–C(5) 1.514(28), C(2)–C(3) 1.465(28), C(3)–C(4) 1.378(33), C(4)–C(11) 1.444(28), C(13)–C(14) 1.335(35), C(13)–Cl(1) 1.741(23), C(14)–C(15) 1.440(32); C(1)–Ir–C(13) 105.1(9), O(9)–Ir–C(4) 101.3(7), C(13)–Ir–C(4) 175.7(9), O(9)–Ir–C(1) 170.4(7).

Chart 2



observe related chemistry involving terminal alkynes which lack a carboxy group capable of coordination to the metal.^{10,11}

The scope of this new vinylidene insertion chemistry with respect to the metal and coordination geometry, as well as the reactivity of the α-halo oxametallacycle ligands, is currently under study.

Acknowledgment. Support by the National Science Foundation and a generous loan of precious metals from Johnson Matthey are gratefully acknowledged. We thank the American Cancer Society Junior Faculty Fellowship Program for support of our programs and Professor Charles Perrin for helpful discussions.

Supporting Information Available: Characterization data for **1-Br**, **1-I**, **4-X** (X = Cl, Br), and **5–8**, details of crystal structure determination, diagram, listings of fractional coordinates, bond distances, bond angles, hydrogen atom coordinates, and thermal parameters for **7** (13 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA951194Z

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