[Cp*IrCl2]2-Assisted C≡C Bond Cleavage with Water: An Experimental and Computational Study

Venugopal Shanmugham Sridevi, Wai Yip Fan, and Weng Kee Leong*

Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543

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Reaction of the dimeric species [Cp*IrCl2]2 with a number of organic substrates carrying a terminal alkyne functionality (RCCH) in the presence of water leads to C≡C bond cleavage to form Cp*IrCl-(CH2R)(CO). The reaction pathway has been studied both experimentally and computationally.
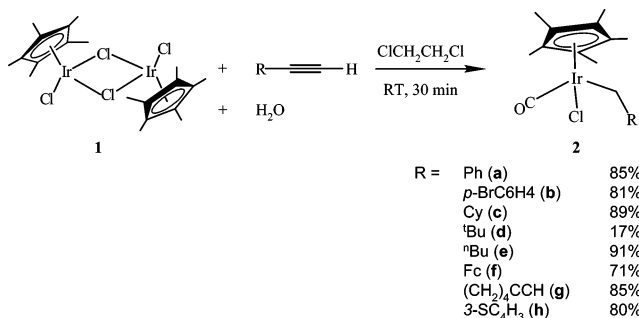
Introduction

Several instances of the metal-assisted C≡C bond cleavage reaction of 1-alkynes with water have been reported; metal systems known include ruthenium,[1] osmium,[2] and iridium.[3] The related reaction of metal-acetylides or vinylidenes with water is also known.[4] For the reactions with 1-alkynes, the C≡C bond cleavage mostly resulted in the formation of complexes containing a carbonyl and an η^1-alkyl with one less carbon atom. In this article, we present our studies on this reaction using the readily accessible dimeric iridium complex [Cp*IrCl2]2, **1**.

Results and Discussion

The reaction of **1** with a number of different 1-alkynes in the presence of water at ambient temperature leads rapidly to complexes of the general formula [Cp*IrCl(CH2R)(CO)], **2**, in modest to high yields (Scheme 1).

The reaction did not occur in the absence of water, and we have found that a similar reaction did not occur with the rhodium analogue, [Cp*RhCl2]2. A similar reaction with Me3SiC≡CH afforded the analogous compound in which the Me3Si group has been replaced by H, viz., [Cp*IrCl(CH3)(CO)], **2i**, in 97% yield; this compound has been obtained by earlier workers via other routes.[5] Interestingly, the same compound was also obtained as the sole product in the reaction with Me3SiC≡CSiMe3. The reaction, however, did not proceed for Ph3SiC≡CH, PhC≡CSiMe3, or the diyne Me3SiC≡CC≡CSiMe3. All the compounds have been completely characterized, and for **2a**, **2f**, **2g**, and **2i** also by single-crystal X-ray crystallographic studies. Compound **2c** was rather unstable; attempts at growing a

Scheme 1

R =   Ph (**a**)   85%
      p-BrC6H4 (**b**)   81%
      Cy (**c**)   89%
      tBu (**d**)   17%
      nBu (**e**)   91%
      Fc (**f**)   71%
      (CH2)4CCH (**g**)   85%
      3-SC4H3 (**h**)   80%

diffraction quality crystal resulted in conversion to [Cp*Ir(CO)-Cl2] via β-hydride elimination.[6]

The ORTEP plot for **2a** is shown in Figure 1, and selected bond parameters together with a common atomic numbering scheme are given in Table 1. Of the four structures, two of them (**2f** and **2g**) showed disorder of the carbonyl and the chloro ligands over each other.

Reaction of **1** with PhCCD showed that the deuterium was not incorporated, pointing to cleavage of the ≡CH bond in the course of the reaction. The source of the carbonyl oxygen was confirmed to be water, as carrying out the reaction in the presence of H2^{18}O afforded [Cp*IrCl(CH2Ph)(C^{18}O)], ^{18}**O-2a**. Water was also the source of the hydrogens in the IrCH2 group, since reaction of **1** with PhCCH in the presence of D2O afforded [Cp*IrCl(CD2Ph)(CO)], ***d*-2a**. Water also accounted for all three hydrogens in the methyl group in **2i**, as carrying out the reaction in the presence of D2O afforded [Cp*IrCl(CD3)(CO)], ***d*-2i**, the identity of which has been established; the Me3Si group was lost as trimethylsilanol, detected as a δ 0.04 resonance in the ^{1}H NMR spectrum of the reaction mixture.[7]

A mechanism, based on a vinylidene intermediate, for such metal-assisted cleavage of C≡C bonds in 1-alkynes has first been studied for the ruthenium system [L3RuCl2(PPh3)], where L3 = CH3CH2CH2N(CH2CH2PPh2)2;[1b] a similar mechanism was also proposed for the iridium system [IrHCl2(PPh3)3][3d] and for the water-soluble [Cp*IrCl2(PAr3)].[3c] The possibility of alkyne hydration to an unbound aldehyde in any part of the reaction pathway was ruled out by the following observations: (a) no PhCH2CHO was observed in the formation of **2a**, (b) dimer **1**

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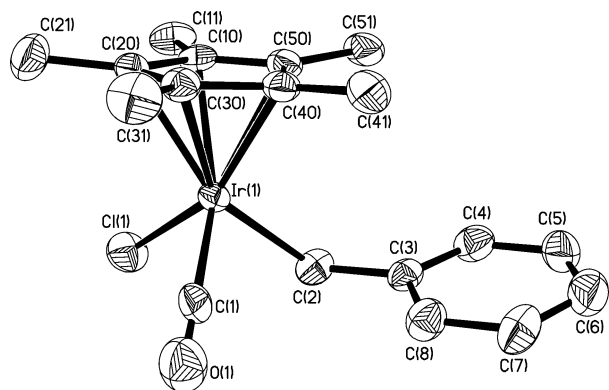(7) Cella, J. A.; Carpenter, J. C. *J. Organomet. Chem.* **1994**, *480*, 23.

Figure 1. ORTEP plot of **2a** (50% thermal ellipsoids drawn, all hydrogen atoms omitted).
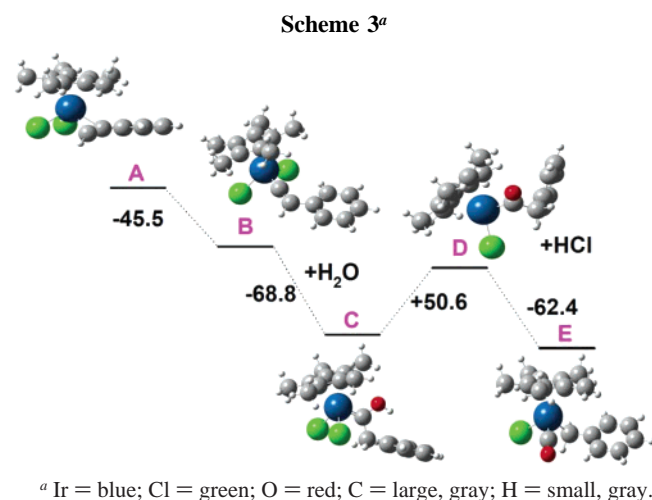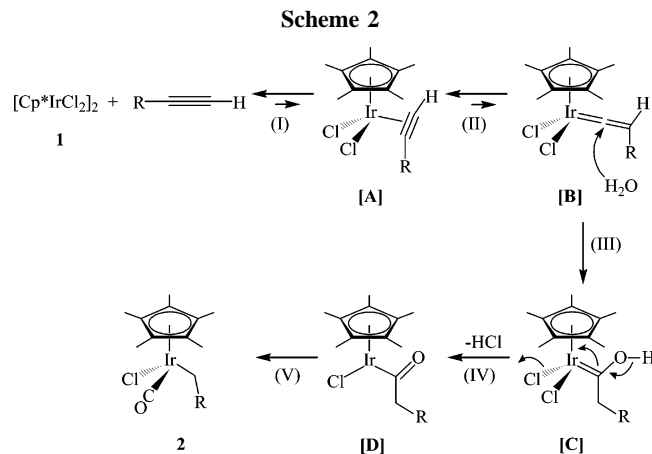
Table 1. Common Atomic Numbering Scheme and Selected Bond Parameters for 2a, 2f, 2g, and 2i

	2a	**2f**[a]	**2g**[a]	**2i**
R	Ph	Fc	$(CH_2)_4CCH$	H
		Bond Lengths (Å)		
Ir(1)−Cl(1)	2.3892(16)	2.378(17)	2.382(2)	2.3637(12)
Ir(1)−C(1)	1.897(8)	1.928(19)	1.825(9)	1.931(6)
Ir(1)−C(2)	2.147(6)	2.135(11)	2.137(4)	2.084(5)
C(1)−O(1)	1.048(9)	1.06(3)	1.177(13)	0.998(7)
C(2)−R	1.497(9)	1.497(15)	1.519(6)	
		Bond Angles (deg)		
Ir(1)−C(1)−O(1)	177.4(7)	173.0(19)	176.8(9)	177.6(6)
Ir(1)−C(2)−R	117.7(4)	117.4(7)	116.8(3)	
Cl(1)−Ir(1)−C(1)	94.1(2)	102.6(18)	93.9(16)	93.64(15)
Cl(1)−Ir(1)−C(2)	83.94(17)	87.6(6)	85.4(3)	85.61(15)

[a] Disorder of Cl and CO.

did not react with PhCH₂CHO to form **2a**, and (c) the reaction of **1** with a mixture of PhCH₂CHO and PhC≡CH in the presence of D₂O afforded only ***d*-2a** but no **2a**; ¹H NMR analysis showed that while all the phenylacetylene was consumed, the aldehyde remained unreacted. Our proposed mechanism for the reaction is given in Scheme 2.

We have also investigated the cycle computationally, at the DFT level of theory with the LANL2DZ basis set; this level of theory has been widely used for computational studies on transition metal sysems.[8] The model reaction studied was that between **1** and PhCCH, and the computed energetics from **A** onward are shown in Scheme 3; the computed reaction free energies are given in kJ mol⁻¹. The formation of **A** is

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Scheme 2

Scheme 3[a]

[a] Ir = blue; Cl = green; O = red; C = large, gray; H = small, gray.

presumably via the monomeric [Cp*IrCl₂]; an equilibrium between **1** and its solvent-stabilized monomeric species has been suggested by earlier workers,[9] and consistent with this, we have found that the dimer to monomer step involved a relatively small $\Delta G°$ (+12.6 kJ mol⁻¹). The binding of the alkyne (step I) was associated with a small, negative $\Delta G°$ (−2.5 kJ mol⁻¹).

The alternative to a vinylidene, viz., the acetylide [Cp*Ir-(Cl)₂(H)(CCPh)], is unlikely; we have computed it to lie at +120.9 kJ mol⁻¹ higher than the vinylidene. In fact, it also lies at a higher energy (+75.4 kJ mol⁻¹) to **A**. The precise pathway for the η²-alkyne to vinylidene rearrangement (step II) is uncertain. However, the fact that there was no deuterium incorporation in the reaction with PhC≡CD ruled out an intramolecular pathway such as a 1,2-shift.[10] A plausible mechanism could be a 1,3-shift or a deprotonation/protonation involving water.[11] However, consistent with earlier proposals,[3c,d] the rearrangement step (II) to the vinylidene **B** was associated with a large, negative $\Delta G°$ (−45.5 kJ mol⁻¹). Since we have found that **1** did not react with PhC≡CH under anhydrous

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conditions, or with LiC≡CPh, it would appear that the driving force for the reaction involved attack of water; the water-catalyzed formation of vinylidene is known.[12] Consequently, we believe that steps I and II probably lie far to the left in the absence of water.

The attack of water at Cα of the vinylidene (step III) is in accord with the LUMO being concentrated at this carbon atom.[10,13] The step involving a formal reductive elimination of HCl (step IV) was associated with a large, positive $\Delta G°$ (+50.6 kJ mol^{-1}), consistent with the formation of a 16-electron species. However, the computational study did not take into account any possible solvation effect of the HCl, which may be expected to lower the associated energetics. Although intermediates **B** and **C** are relatively uncommon Ir(V) species, nevertheless we have found that when **1** was reacted with PhC≡CH in the presence of methanol, a species that can be identified spectroscopically as [Cp*Ir{=COCH₃(CH₂Ph)}Cl₂], **3**, was formed (together with another as-yet unidentified species that increased with time); the ¹H NMR and FAB-MS data were consistent with the formulation, together with the observation of a singlet signal at 171 ppm in the ¹³C NMR assignable to the presence of an Ir=C moiety. The use of PhCCD in the presence of MeOH did not result in any incorporation of deuterium, while reactions in the presence of d_3- or d_4-methanol afforded [Cp*Ir{=COCD₃(CH₂-Ph)}Cl₂], d_3-**3**, or [Cp*Ir{=COCD₃(CD₂Ph)}Cl₂], d_5-**3**, respectively; the formation of d_3-**3** further confirmed the source of the protons in the CH₂ moiety as the solvent (CD₃OH). Although attempts at the isolation of pure **3** were unsuccessful, as it turned out to be rather unstable, we were able to characterize spectroscopically and analytically the ᵗBu analogue, [Cp*Ir{=COCH₃(CH₂ᵗBuPh)}Cl₂], **3a**, from the analogous reaction employing ᵗBuC≡CH. The identitication of **3a**, we believe, corroborates the intermediacy of **C** in the reaction.

The final step (V), a migratory deinsertion, is energetically favorable and is consistent with observation that deinsertion at iridium is generally more favorable than on rhodium.[14] Such deinsertion has been observed in other related systems.[15]

Conclusion

We have reported here the very facile reaction of the readily available dimeric species [Cp*IrCl₂]₂ with 1-alkynes in the presence of water leading to C≡C bond cleavage to form compounds of the general formula [Cp*IrCl(CH₂R)(CO)]. This represents a very useful way to access thermally unstable transition metal alkyls. The mechanistic pathway has been studied using a combination of experimental and computational means, and the proposed mechanism involved redox chemistry between Ir(III) and Ir(V) intermediates.

Experimental Section

General Procedures. All reactions and manipulations were performed under argon using standard Schlenk techniques. Solvents

were purified, dried, distilled, and stored under nitrogen prior to use, except for ClCH₂CH₂Cl, which was used as supplied unless otherwise stated. Oxygen-18-labeled water (95 atom % ¹⁸O) was purchased from Aldrich and used as received. ¹H NMR spectra were recorded on a Bruker ACF300 or AV300 NMR spectrometer as CDCl₃ solutions; chemical shifts reported were referenced against the residual proton signals of the solvent. Mass spectra were obtained on a Finnigan MAT95XL-T spectrometer in a 3NBA matrix (FAB) or a Finnigan MAT LCQ spectrometer with MeOH as solvent (ESI). All elemental analyses were performed by the microanalytical laboratory at NUS. [Cp*IrCl₂]₂, **1**, was prepared according to the published method.[6] All other reagents were from commercial sources and used without further purification.

Reaction of 1 with Phenyl Acetylene. A dichloroethane solution (4 mL) of [Cp*IrCl₂]₂, **1** (36.3 mg, 45.6 μmol), and phenylacetylene (10 μL, 91.2 μmol) was stirred at room temperature for 0.5 h. The solvent was then removed under reduced pressure and the residue obtained was dissolved in the minimum amount of dichloromethane and chromatographed on silica gel TLC plates. Elution with hexane/CH₂Cl₂ (1:1, v/v) yielded [Cp*IrCl(CH₂Ph)(CO)], **2a**, as a yellow solid.

A similar procedure was employed with the other alkynes. Product yields and characterization data are given in Table 2.

Reaction of 1 with Phenyl Acetylene in Methanol. A dichloroethane solution (1 mL) of **1** (36.3 mg, 45.6 μmol), PhCCH (10 μL, 91.2 μmol), and methanol (0.1 mL) was allowed to stand at room temperature for 0.5 h. The solvent was then removed under reduced pressure and redissolved in CDCl₃. Analysis of the mixture showed the presence of **3** and a small quantity of an unidentified product.

¹H NMR (δ, CDCl₃): 1.67 (s, 15H, Cp*), 4.64 (s, 2H, CH₂), 4.82 (d, 3H, OCH₃), 7.16−7.52 (m, aromatic). FAB-MS: 532 [M]⁺, 497 [M − Cl]⁺.

An analogous reaction using ᵗBuC≡CH afforded, after removal of solvent and volatiles under reduced pressure and extraction with ether, an orange-yellow solid identified as [Cp*Ir(=C(OCH₃)(CH₂-Buᵗ))Cl₂], **3a**. Yield = 86%.

¹H NMR (δ, CDCl₃): 1.67 (s, 15H, Cp*), 1.02 (s, 9H, CH₃), 3.23 (s, 2H, CH₂), 4.88 (s, 3H, OCH₃). ¹³C NMR (δ, CDCl₃): 292.7 (s, Ir=C), 92.9 (s, Cp*), 72.7 (s, OCH₃), 69.1 (s, CH₂), 30.3 (s, C(CH₃)₃), 8.9 (s, Cp*), 1.0 (s, CH₃). FAB-MS: 512 [M]⁺, 477 [M − Cl]⁺. Anal. Calcd for C₁₇H₂₉Cl₂O₁Ir₁: C, 39.84; H, 5.70. Found: C, 40.09; H, 5.73.

X-ray Crystallographic Studies. Crystals were grown from dichloromethane/hexane solutions and mounted on quartz fibers. X-ray data were collected on a Bruker AXS APEX system, using Mo Kα radiation, at 223 K with the SMART suite of programs.[16] Data were processed and corrected for Lorentz and polarization effects with SAINT[17] and for absorption effects with SADABS.[18]

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Table 2. Product Yields and Characterization Data

product	alkyne	ν_{CO} (CH$_2$Cl$_2$)/cm^{-1}	^{1}H NMR (δ, CDCl$_3$)	FAB-MS [M]$^+$, [M − Cl]$^+$	elemental analysis found (calcd)
2a	PhCCH	2011(vs)	1.79 (s, 15H, Cp*), 3.02 (d, 1H, $^2J_{HH}$ = 9.3 Hz, CH$_2$), 3.98 (d, 1H, CH$_2$), 6.94−6.99 (m, 1H, aromatic), 7.13−7.26 (m, 4H, aromatic)	482, 447	C, 45.27 (44.85) H, 4.28 (4.60)
d-**2a**	PhCCH	2010(vs)	1.79 (s, 15H, Cp*), 6.94−6.99 (m, 1H, aromatic), 7.13−7.26 (m, 4H, aromatic)	484, 449	C, 44.81 (44.66) H, 4.39 (4.16)
^{18}O-**2a**	PhCCH	2011(w), 1968(vs)	1.79 (s, 15H, Cp*), 3.02 (d, 1H, $^2J_{HH}$ = 9.4 Hz, CH$_2$), 3.98 (d, 1H, CH$_2$), 6.94−6.99 (m, 1H, aromatic), 7.13−7.26 (m, 4H, aromatic)	484, 449	
2b	*p*-BrC$_6$H$_4$CCH	2011(vs)	1.80 (s, 15H, Cp*), 3.02 (d, 1H, *J* = 9.2 Hz, CH$_2$), 3.78 (d, 1H, CH$_2$), 7.11−7.41 (m, 4H, aromatic)	561	C, 39.03 (38.54) H, 4.18 (3.77)
2c	CyCCH	2003(vs)	1.83 (s, 15H, Cp*), 1.92 (s, 2H, CH$_2$), 1.05−1.34 (m, 2H, Cy), 1.55−1.90 (m, 8H, Cy), 2.52−2.58 (m, 1H, C−H, Cy)	488, 453	C, 47.00 (47.49) H, 6.26(6.6)^a
2d	^{t}BuCCH	1995(vs)	1.82 (s, 15H, Cp*), 2.02 (d, 1H, $^2J_{HH}$ = 9.6 Hz, CH$_2$), 2.73 (d, 1H, CH$_2$), 1.01 (s, 9H, CH$_3$)	462, 427	low yield
2e	^{n}BuCCH	2004(vs)	1.85 (s, 15H, Cp*), 2.49−2.41 (m, 2H, CH$_2$), 1.67−1.62 (m, 2H, CH$_2$), 1.35−1.32 (m, 4H, CH$_2$), 0.88 (t, 3H, CH$_3$)	461, 427	C, 43.50 (43.46) H, 6.10 (6.15)
2f	FcCCH	2007(vs)	1.79 (s, 15H, Cp*), 4.19 (s, 5H, Cp), 4.27 (m, 2H, Cp), 4.52 (m, 2H, Cp), 5.22 (d, 1H, $^2J_{HH}$ = 1.1 Hz, CH$_2$), 5.44 (d, 1H, CH$_2$)	590, 555	C, 45.22 (44.79) H, 4.38 (4.44)
2g	HCC(CH$_2$)$_4$CCH	2116(w), 2004(vs)	1.85 (s, 15H, Cp*), 1.41−1.69 (m, 8H, CH$_2$), 1.92−1.93 (m, 1H, CH$_2$), 1.99 (s, 1H, ≡C−H), 2.32−2.42 (m, 1H, CH$_2$).	487, 453	C, 44.82 (44.48) H, 5.64 (5.39)
2h	3-C$_4$H$_3$SCCH	2007(vs)	1.76 (s, 15H, Cp*), 2.91 (d, 1H, $^2J_{HH}$ = 10.2 Hz, CH$_2$), 3.96 (d, 1H, CH$_2$), 6.83 (m, 1H, thiophene), 7.01−7.20 (m, 1H, thiophene), 7.43−7.67 (m, 1H, thiophene)	452	C, 41.54 (41.24) H, 4.17 (4.65)^b
2i	Me$_3$SiCCH	2010(vs), 1962(w)	1.87 (s, 15H, Cp*), 1.07 (s, 3H, CH$_3$)	406, 371	C, 35.50 (35.50) H, 4.47 (4.56)

^{a} Based on 0.5 hexane solvate. Presence of hexane in sample verified by ^{1}H NMR. ^{b} Based on 0.25 hexane solvate.

Table 3. Crystal Data and Structure Refinement for 2a and 2d−f

	2a	**2f**	**2g**	**2i**
empirical formula	C$_{18}$H$_{22}$ClIrO	C$_{22}$H$_{26}$ClFeIrO	C$_{18}$H$_{26}$ClIrO	C$_{12}$H$_{18}$ClIrO
fw	482.01	589.93	486.04	405.91
cryst system	monoclinic	triclinic	triclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	14.0317(5)	7.5593(5)	7.0618(6)	7.6284(10)
b, Å	7.0962(3)	10.4598(8)	10.9572(9)	8.0215(11)
c, Å	18.1574(7)	13.2612(9)	12.0565(10)	12.0085(16)
α, deg	90	98.916(2)	94.249(2)	77.503(2)
β, deg	110.5740(10)	103.329(2)	105.388(2)	80.148(2)
γ, deg	90	98.601(2)	96.320(2)	66.855(2)
volume, Å^3	1692.65(11)	989.07(12)	888.78(13)	656.63(15)
Z	4	2	2	2
density (calcd), Mg/m^3	1.891	1.981	1.816	2.053
absorp coeff, mm^{-1}	8.042	7.597	7.659	10.344
F(000)	928	572	472	384
cryst size, mm^3	0.24 × 0.12 × 0.04	0.12 × 0.06 × 0.01	0.25 × 0.21 × 0.08	0.28 × 0.22 × 0.12
no. of reflns collected	26 021	10 685	10 451	9453
no. of indep reflns	4983 [*R*(int) = 0.0413]	4042 [*R*(int) = 0.0555]	4648 [*R*(int) = 0.0265]	2683 [*R*(int) = 0.0278]
completeness, % (to θ, deg)	96.5 (30.50)	99.9 (26.37)	90.3 (29.92)	100.0 (26.37)
max. and min. transmn	0.74 and 0.25	0.93 and 0.46	0.58 and 0.25	0.37 and 0.16
no. of data/restraints/params	4983/0/195	4042/3/250	4648/8/227	2683/0/197
goodness-of-fit on F^2	1.292	1.318	1.062	1.049
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0463, wR2 = 0.0942	R1 = 0.0676, wR2 = 0.1304	R1 = 0.0285, wR2 = 0.0644	R1 = 0.0202, wR2 = 0.0501
R indices (all data)	R1 = 0.0493, wR2 = 0.0955	R1 = 0.0741, wR2 = 0.1330	R1 = 0.0318, wR2 = 0.0658	R1 = 0.0214, wR2 = 0.0508
largest diff peak and hole, e Å^{-3}	2.216 and −2.354	2.298 and −5.635	1.730 and −0.900	1.055 and −0.467

Structural solution and refinement were carried out with the SHELXTL suite of programs.[19] Crystal and refinement data are summarized in Table 3.

The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. Organic hydrogen atoms were placed in calculated positions and refined with a riding model. The structures of **2f** and **2g** exhibited disorder of the CO with the Cl ligands. These were modeled with two alternative sites each, with appropriate restraints placed on bond and thermal parameters and occupancies summed to unity. All non-hydrogen atoms were given anisotropic displacement parameters in the final model.

Computational Studies. The reaction energetics for the reaction of **1** with PhCCH was studied using DFT theory together with the LANL2DZ basis set. Spin-restricted calculations were used for determining the structures of the organic, inorganic, and organometallic reactants, intermediates, and products, fully optimized at the DFT/LANL2DZ level. Harmonic frequencies were calculated at the optimized geometries to characterize stationary points as equilibrium structures, with all real frequencies, and to evaluate zero-point energy (ZPE) correction. All calculations were performed using the Gaussian 03 suite of programs.[20]

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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