

Binuclear Complexes as Models for Adjacent-Metal Involvement in C–H Bond-Cleavage and C–C Bond-Formation Steps Relevant to Fischer–Tropsch Chemistry

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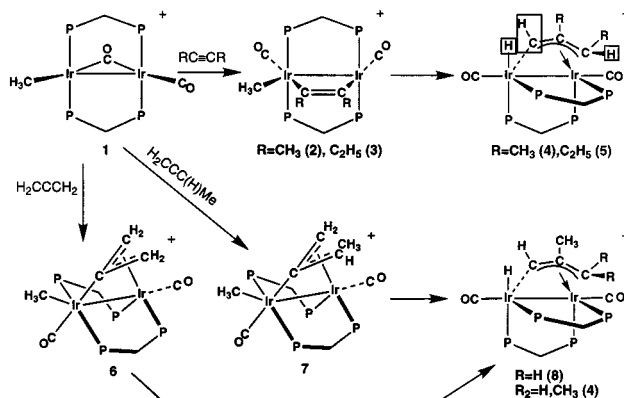
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Received November 17, 1997

α -Hydrogen elimination reactions are not common in mono-nuclear, late-metal complexes but occur readily and reversibly on a variety of metal surfaces (including those of late metals), yielding alkylidene and alkylidyne fragments from surface-bound alkyls.¹ Such conversions may be of significance in C–C bond formation, as suggested by the work of Maitlis and co-workers,² in which vinyl groups (which can result from the combination of methyne and methylene fragments on a metal surface) appear to be important in C–C chain growth in Fischer–Tropsch (FT) chemistry, via migration to adjacent methylene units. In this communication we present results of studies aimed at modeling the involvement of surface-bound methyl groups, in which we demonstrate that the methyl group in the model compound, $[\text{Ir}_2(\text{CH}_3)(\text{CO})_2(\text{dppm})_2][\text{SO}_3\text{CF}_3]$ (**1**) (dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$), undergoes facile activation upon reaction with alkynes or allenes, leading to a series of vinylcarbene products. Labeling studies demonstrate the involvement of at least two pathways, differing in the sequence of C–H activation and C–C bond-formation steps.

Compound **1** reacts with internal alkynes such as 2-butyne and 3-hexyne to give the dark red products $[\text{Ir}_2(\text{CH}_3)(\text{CO})_2(\mu\text{-RC}\equiv\text{CR})(\text{dppm})_2][\text{SO}_3\text{CF}_3]$ (**2**), **3**),³ assumed to have the alkyne-bridged structures shown in Scheme 1, on the basis of the spectral similarities with the dimethyl acetylenedicarboxylate-bridged species.⁴ Over a 24 h period at ambient temperature, **2** and **3** rearrange to the yellow vinylcarbene products $[\text{Ir}_2\text{H}(\text{CO})_2(\mu\text{-}\eta^1, \eta^3\text{-CHC(R)C(H)R})(\text{dppm})_2][\text{SO}_3\text{CF}_3]$ (**4**), **5**),⁵ resulting formally from the activation of two C–H bonds of the methyl group, C–C bond formation between the resulting methyne carbon and one of the acetylenic carbons, and H transfer to the other acetylenic carbon. ¹³C NMR spectra of a sample of **4**, obtained from ¹³CH₃-labeled compound **1** confirm that the methyl carbon ends up at the bridgehead position. This structure type has been confirmed by an X-ray study on **5**,⁶ as shown in Figure 1. The fragments, resulting from the original

Scheme 1^a



^a In compounds **4** and **5** the original methyl ligand fragments are shown in boxes.

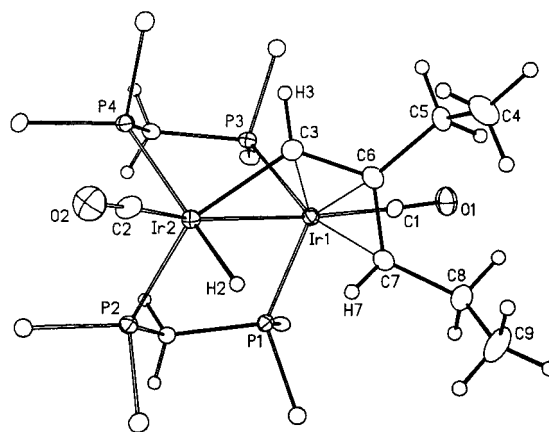


Figure 1. Perspective view of the cation of **5**; only the ipso carbons of the phenyl groups are shown. Important bond lengths (Å) and angles (deg): Ir(1)–Ir(2) = 2.7623(7); Ir(1)–C(3) = 2.207(6); Ir(1)–C(6) = 2.233(6); Ir(1)–C(7) = 2.220(7); Ir(2)–C(3) = 2.064(7); C(3)–C(6) = 1.440(10); C(6)–C(7) = 1.431(9); Ir(1)–C(3)–Ir(2) = 80.5(2); Ir(2)–C(3)–C(6) = 126.0(5); C(3)–C(6)–C(7) = 116.9(6).

methyl group, are shown within boxes in Scheme 1 and are labeled C(3)H(3), H(2), and H(7) in Figure 1. The vinylcarbene moiety, η^1 -bound to Ir(2) and η^3 -bound to Ir(1), can equally well be considered as a metallallyl moiety, and both formulations have previously been considered.⁷

Compound **1** also reacts with allene and methylallene to initially yield adducts in which the allene moieties bridge the metals, being η^1 -bound to one metal through the central carbon of the allene group and η^3 -bound to the other metal, as shown for compounds **6**⁸ and **7** in Scheme 1. This structure type has been confirmed by an X-ray determination of compound **6**,⁹ shown in Figure 2. These products are not unlike the alkyne-bridged compounds, giving a geometry at Ir(1) much like that proposed in **2** and **3**, but having a *cis*-phosphine arrangement at Ir(2), at which η^3 -

(6) Crystal data of **5**: triclinic, $P\bar{1}$; $a = 12.599(2)$ Å, $b = 14.284(3)$ Å, $c = 18.871(4)$ Å, $\alpha = 88.50(2)^\circ$, $\beta = 84.946(15)^\circ$, $\gamma = 89.16(2)^\circ$; $V = 3381.4(12)$ Å³; $Z = 2$; $D_{\text{calc}} = 1.610$ g cm⁻³; $\mu(\text{MoK}\alpha) = 41.16$ cm⁻¹; $T = -50$ °C; $\lambda(\text{MoK}\alpha) = 0.71073$ Å; 11827 independent reflections measured, 8426 observed ($I > 2\sigma(I)$); 808 variables; $R_1(F) = 0.0364$ (observed data), $wR_2(F^2) = 0.0958$ (all data).

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(1) (a) Zäara, F. *Chem. Rev.* **1995**, *95*, 2651. (b) Driessen, M. D.; Grassian, V. H. *J. Am. Chem. Soc.* **1997**, *119*, 1697.

(2) See, for example: (a) Turner, M. L.; Long, H. C.; Shenton, A.; Byers, P. K.; Maitlis, P. M. *Chem. Eur. J.* **1995**, *1*, 549. (b) Maitlis, P. M.; Long, H. C.; Quyoum, R.; Turner, M. L.; Wang, Z.-Q. *Chem. Commun.* **1996**, 1.

(3) Spectroscopic data for **2**: ¹H NMR (400 MHz, CD₂Cl₂) δ : 3.91 (m, 2H), 3.24 (m, 2H), 1.33 (b, 3H), 0.76 (b, 3H), 0.47 (t, 3H); ³¹P NMR δ : 10.4 (m), -9.4 (m). Anal. Calcd for Ir₂SP₄F₃O₅C₅₈H₅₃: C, 48.80; H, 3.75. Found: C, 49.02; H, 3.74.

(4) Torkelson, J. R.; McDonald, R.; Cowie, M. Manuscript in preparation. (5) Spectroscopic data for **4**: ¹H NMR (400 MHz, CD₂Cl₂) δ : 8.79 (m, 1H), 7.12 (m, 1H), 5.83 (m, 1H), 4.60 (m, 1H), 3.78 (m, 1H), 3.29 (m, 1H), 2.72 (d, 3H), 1.42 (bm, 3H), -11.25 (m, 1H); ¹³C NMR (natural abundance) δ : 170.85 (m, CO), 168.2 (b, CO), 138 (t, ²J_{C-P} = 63.5 Hz, $\mu\text{-}\eta^1\text{-}\eta^3\text{-HCC}(\text{CH}_3)=\text{CHCH}_3$), 110 (s, $\mu\text{-}\eta^1\text{-}\eta^3\text{-HCC}(\text{CH}_3)=\text{CHCH}_3$), 64 (t, $\text{Ph}_2\text{PCH}_2\text{PPh}_2$), 56 (m, $\mu\text{-}\eta^1\text{-}\eta^3\text{-HCC}(\text{CH}_3)=\text{CHCH}_3$), 42 (t, $\text{Ph}_2\text{PCH}_2\text{PPh}_2$), 24 (s, $\mu\text{-}\eta^1\text{-}\eta^3\text{-HCC}(\text{CH}_3)=\text{CHCH}_3$), 18 (s, $\mu\text{-}\eta^1\text{-}\eta^3\text{-HCC}(\text{CH}_3)=\text{CHCH}_3$); ³¹P NMR δ : -5.8 (m), -6.0 (m), -34.3 (m), -37.8 (m). Anal. Calcd for Ir₂SP₄F₃O₅C₅₉H₅₈: C, 48.80; H, 3.75. Found: C, 48.30; H, 3.58. Spectroscopic data for compound **5** are similar.

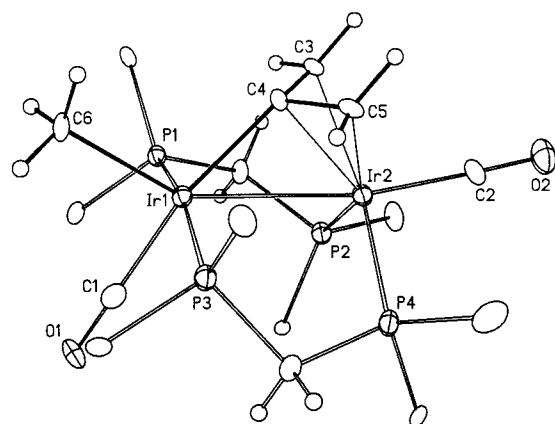


Figure 2. Perspective view of the cation of **6**; only the ipso carbons of phenyl groups are shown. Important bond lengths (Å) and angles (deg): Ir(1)–Ir(2) = 2.844(1); Ir(1)–C(4) = 2.09(2); Ir(2)–C(3) = 2.20(2); Ir(2)–C(4) = 2.12(2); Ir(2)–C(5) = 2.21(2); C(3)–C(4) = 1.41(2); C(4)–C(5) = 1.44(2); C(3)–C(4)–C(5) = 108.4(15).

binding of the iridaallyl group occurs. This allene binding mode has been observed but is not common.¹⁰ NMR studies on **6** confirm that the structure observed in the crystal is maintained in solution.

As was the case for the alkyne adducts (**2**, **3**), the allene adducts **6** and **7** are the kinetic products and rearrange slowly¹¹ to the vinylcarbene species $[\text{Ir}_2\text{H}(\text{CO})_2(\mu\text{-}\eta^1, \eta^3\text{-CHC}(\text{Me})\text{CR}_2)(\text{dppm})_2][\text{SO}_3\text{CF}_3]$ ($\text{R} = \text{H}$ (**8**), $\text{R}_2 = \text{H}$, Me (**4**)) at ambient temperature. These compounds are analogous to the double C–H activation products (**4** and **5**) that resulted in the alkyne reactions and display the characteristic methyne ¹H resonance at ca. δ 8.7, and the characteristic ³¹P{¹H} spectrum. (Note that compound **4** results both from the reactions of **1** with 2-butyne and methylallene.) In the methylallene reaction two isomers of **4** are observed, resulting from a *cis* or *trans* positioning of the methyl groups on the vinylcarbene.

Although vinylcarbene compounds, analogous to compounds **4**, **5**, and **8** are known,⁷ their generation from a methyl complex and alkynes or allenes is unprecedented and deserves comment. A unified proposal for the formation of these vinylcarbene products, that is also consistent with the results in the reactions of **1** with CO, SO₂, and other groups,¹² is summarized in Scheme 2.¹³ We propose that the alkyne (**2**, **3**) and the allene (**6**, **7**) adducts rearrange to the methylene-bridged hydride products **A**, having the unsaturated substrate *terminally* bound to one metal. A number of species having this or a related geometry have been characterized.^{12b} Migratory insertion involving the unsaturated substrate and the hydride ligand would yield the substituted vinyl

(8) Spectroscopic data for **6**: ¹H NMR (400 MHz, CD₂Cl₂) δ : 5.46 (m, 2H), 5.09 (m, 2H), 4.23 (b, 2H), 3.52 (b, 2H), 1.18 (t, 3H); ¹³C NMR (natural abundance) δ : 179.2 (t, CO), 171.2 (b, CO), 127.3 (b, $\eta^1\text{-}\eta^3\text{-H}_2\text{C}=\text{C}=\text{CH}_2$), 61.3 (m, $\eta^1\text{-}\eta^3\text{-H}_2\text{C}=\text{C}=\text{CH}_2$), –31.1 (t, ²J_{C–P} = 3.3 Hz, CH₃); ³¹P NMR δ : –16.7 (m). Anal. Calcd for Ir₂SP₄F₃O₅C₅₇H₅₁: C, 48.43; H, 3.64. Found: C, 48.23; H, 3.50.

(9) Crystal data of **6**: triclinic, $P\bar{1}$; $a = 10.4603(1)$ Å, $b = 14.2406(1)$ Å, $c = 38.7838(4)$ Å, $\alpha = 91.887(1)^\circ$, $\beta = 97.732(1)^\circ$, $\gamma = 90.281(1)^\circ$; $V = 5721.39(9)$ Å³; $Z = 4$; $D_{\text{calc}} = 1.674$ g cm^{–3}; $\mu(\text{MoK}\alpha) = 48.82$ cm^{–1}; $T = -60$ °C; $\lambda(\text{MoK}\alpha) = 0.71073$ Å; 23 466 independent reflections measured, 10 928 observed ($I > 2\sigma(I)$); 1312 variables; $R_1(F) = 0.0867$ (observed data), $wR_2(F^2) = 0.1853$ (all data).

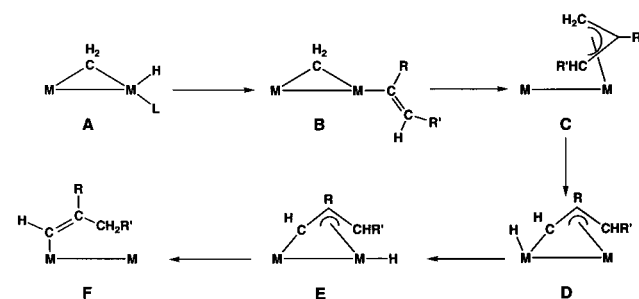
(10) See, for example: (a) Chacon, S. T.; Chisholm, M. H.; Folting, K.; Huffman, J. C.; Hampden-Smith, M. J. *Organometallics* **1991**, *10*, 3722. (b) Coborn, R. E.; Dyke, A. F.; Knox, S. A. R.; Mead, K. A.; Woodward, P. J. *Chem. Soc., Dalton Trans.* **1983**, 2099.

(11) Rearrangement of compounds **6** and **7** to products **8** and **4** takes 24 and 2 h, respectively, with some decomposition and reformation of **1**.

(12) (a) Antwi-Nsiah, F.; Cowie, M. *Organometallics* **1992**, *11*, 3157. (b) Torkelson, J. R.; McDonald, R.; Antwi-Nsiah, F.; Cowie, M.; Pruis, J. G.; Jalkanen, K. J.; DeKock, R. Manuscript in preparation.

(13) In the alkyne reactions it is also possible that a direct insertion of the alkyne into the $\mu\text{-CH}_2$ group occurs to give a bridged $-\text{CH}_2\text{C}(\text{R})=\text{C}(\text{R})-$ moiety, followed by a 1,3-sigmatropic shift of one hydrogen, to give the vinylcarbene products.

Scheme 2^a



^a L = RC≡CR'; H₂C=C=CHR' (R' = H, CH₃): for allenes, R = CH₃ in scheme.

products **B**; such insertions are common for alkynes and have also been observed for allenes¹⁴ (the observation of two isomers of **4** is consistent with this proposal, resulting from H-transfer to each face of the C=CH₂ moiety). A vinyl-to-methylene migration, as proposed by Maitlis,² would yield an allyl product, possibly having a structure such as **C**, and carbon–hydrogen bond cleavage at the *least substituted end* of the allyl group, by the adjacent metal, would yield the final vinylcarbene products (**D**).

Scheme 2 considers only one possible route for the formation of the 2-methylallyl intermediate (**C**) in the reaction of **1** with allene. Another route, involving direct methyl migration to the central carbon (C(4)) of the metallallyl unit, is suggested by the close proximity of these groups to Ir(1) in the structure of **6**, as shown in Figure 2, and has been confirmed by labeling studies. Therefore, reaction of ¹³CH₃-labeled **1** with allene yields **8** in which the label is distributed over the α -, 2-methyl-, and γ -positions in a 1:ca.2:1 ratio. Enrichment at the 2-methyl position results from direct methyl migration onto the central allylic carbon in **6** to yield the 2-methyl allyl intermediate **C**, whereas the methylene-hydride route, shown in Scheme 2, places the label at the $\mu\text{-CH}_2$ group of **A** and **B**, which upon migratory insertion of the isopropenyl ligand would give ¹³C at one end of the 2-methylallyl group. C–H bond cleavage in this intermediate would be equally likely at *either* end of this symmetrical allyl ligand, scrambling the label equally between the α - and γ -sites of **D**. To our knowledge this is the first example of direct methyl transfer to a $\mu\text{-}\eta^1, \eta^3$ -bound allene group.

One of the key transformations in the Maitlis proposal, the allyl-to-vinyl isomerization, has little literature precedent.¹⁵ Scheme 2 suggests a plausible mechanism for this isomerization, in which the conversion of species **C** to **D** could be followed by migration of the hydride to the adjacent metal (species **E**) and by subsequent transfer to the terminal carbon of the vinylcarbene moiety, yielding the vinyl complex (**F**).

The transformations described in this paper, we feel, offer useful insights into the oligomerization steps in Fischer–Tropsch chemistry and offer additional support for the importance of vinyl groups as proposed by Maitlis.

Acknowledgment. The authors thank the Natural Sciences and Engineering Research Council of Canada (NSERC) and the University of Alberta for financial support, NSERC and the U of A for graduate scholarships (to J.R.T.), and Dr. James F. Britten (McMaster University) for X-ray data collection on compound **6**.

Supporting Information Available: Listings of crystal data, data collection, solution and refinement, complete atomic coordinates, bond distances and angles, and anisotropic thermal parameters for compounds **5** and **6** (42 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(14) Sterenberg, B. T.; McDonald, R.; Cowie, M. *Organometallics* **1997**, *16*, 2297.

(15) Two known reports are (a) Deeming, A. J.; Shaw, B. L.; Stainbank, R. E. *J. Chem. Soc. A* **1971**, 374. (b) Wang, L.-S.; Cowie, M. *Can. J. Chem.* **1995**, *73*, 1058.