Supplementary Materials: Successive Activation of C–H and C–O Bonds of Vinyl Ethers by a Diphosphine and Hydrido-Bridged Diiridium Complex

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Crystallography: Experimental Details

The crystal data and experimental details for **3**, **4**, and **5** are summarized in Table 1. Diffraction data for **3**, **4**, and **5** were obtained with a Rigaku RAXIS RAPID instrument. Reflection data for **3**, **4**, and **5** were corrected for Lorentz and polarization effects. Empirical absorption corrections were applied. The structures of **3**, **4**, and **5** were solved by heavy-atom Patterson method[1, 2] and refined anisotropically for non-hydrogen atoms by full-matrix least-squares calculations. Atomic scattering factors and anomalous dispersion terms were taken from the literature.[3] In **4**, two carbon atoms of -vinylidene group exhibited positional disorder. Thus, population parameters of C28, C29, C30, and C31 were refined. This resulted in occupancies of 61% (molecule A with C28 and C29) and 39% (molecule B with C30 and C31). The hydrogen atoms attached to the disordered -vinylidene group in **4** were not located. The location of the metal hydrides in **3** and **4** could not be determined. Other hydrogen atoms were located on the idealized positions. The calculations were performed using the program system CrystalStructure.[4, 5] COD-3000257, 3000258, and 3000259 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.crystallography.net/search.html.

Table S1. Crystal Data and Structure Refinement Parameter for **3**, **4** and **5**.

	3	**4**	**5**
	Description of Crystal		
color, habit	yellow, block	orange, block	orange, block
max cryst dimens (mm)	0.30 × 0.15 × 0.10	0.35 × 0.15 × 0.15	0.35 × 0.30 × 0.20
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$ (#14)	$P2_1/c$ (#14)	$P2_1/c$ (#14)
a (Å)	9.8123(3)	17.2066(5)	10.63646(19)
b (Å)	18.7073(6)	13.4578(3)	19.4945(4)
c (Å)	19.0731(5)	17.4402(4)	15.9469(3)
α (deg)	90	90	90
β (deg)	91.8175(8)	118.3955(8)	102.8964(7)
γ (deg)	90	90	90
V (Å^3)	3499.34(18)	3552.61(16)	3223.22(10)
Z	4	4	4
formula	$C_{30}H_{51}O_4F_3P_2SIr_2$	$C_{30}H_{51}O_4F_3P_2SIr_2$	$C_{28}H_{47}O_3F_3P_2SIr_2$
fw	1011.17	1011.17	967.12
D_{calc} (g cm^{-3})	1.919	1.890	1.993
	Data Collection		
radiation (λ, Å)	MoKα (= 0.71075Å)	MoKα (= 0.71075Å)	MoKα (= 0.71075Å)
temp (K)	173	173	173
no. of data images		55	
ω oscillation range (χ = 45.0) (deg)	130.0–190.0 (ϕ = 30.0)	130.0–190.0 (ϕ = 30.0)	130.0–190.0 (ϕ = 0.0)
exposure rate (s/deg)	120.0	180.0	240.0
ω oscillation range (χ = 45.0) (deg)	0.0–160.0 (ϕ = 210.0)	0.0–160.0 (ϕ = 180.0)	0.0–160.0 (ϕ = 180.0)
exposure rate (s/deg)	120.0	180.0	240.0
detector position (mm)	127.40	127.40	127.40
pixel size (mm)	0.100	0.100	0.100
$2\theta_{max}$ (deg)	54.92	54.94	54.96
no. of reflns measd	33309	33301	31455
	Structure Determination		
no. of observations	6039	6354	6798
no. of variables	428	449	399
refln/param ratio	14.11	14.15	17.04
transmn factor	0.101−0.458	0.131−0.315	0.060−0.183
R (I > 2.00σ(I))[a]	0.0536	0.0411	0.0314
Rw (I > 2.00σ(I))[a]	0.0860[b]	0.0629[c]	0.0453[d]
goodness of fit indicator	1.003	1.003	1.007

[a] $R = ||F_o| - |F_c||/|F_o|$, $R_w = [w(|F_o| - |F_c|)^2/wF_o^2]^{1/2}$ [b] $1/[0.0036F_o^2+1.0000 (F_o^2)]$ [c] $1/[0.0020F_o^2+1.0000 (F_o^2)]$ [d] $1/[0.0002F_o^2+1.0000 (F_o^2)]$.

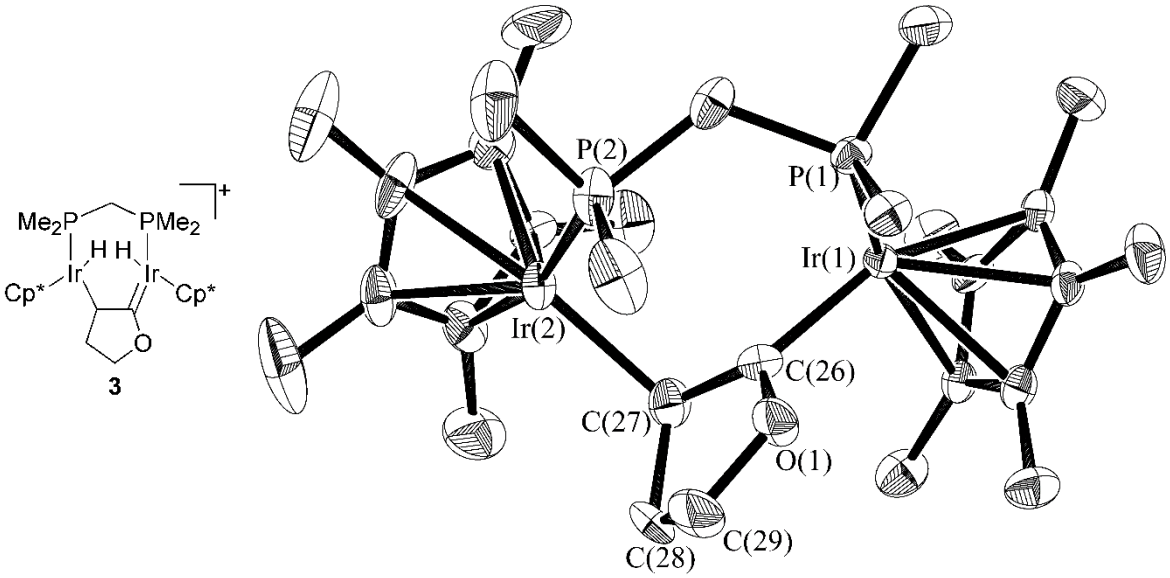

Figure S1. ORTEP drawing of cationic part of **3**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ir(1)−Ir(2) = 4.1838(5), Ir(1)−P(1) = 2.239(2), Ir(2)−P(2) = 2.252(3), Ir(1)−C(26) = 1.978(11), Ir(2) −C(27) = 2.206(11), O(1)−C(26) = 1.394(13), C(26)−C(27) = 1.421(16), C(27)−C(28) = 1.562(16), P(1)−Ir(1)−C(26) = 91.2(3), P(2)−Ir(2)−C(27) = 105.2(3), Ir(1)−C(26)−O(1) = 117.6(8), Ir(1)−C(26)−C(27) = 131.2(8), O(1)−C(26)−C(27) = 109.4(9).

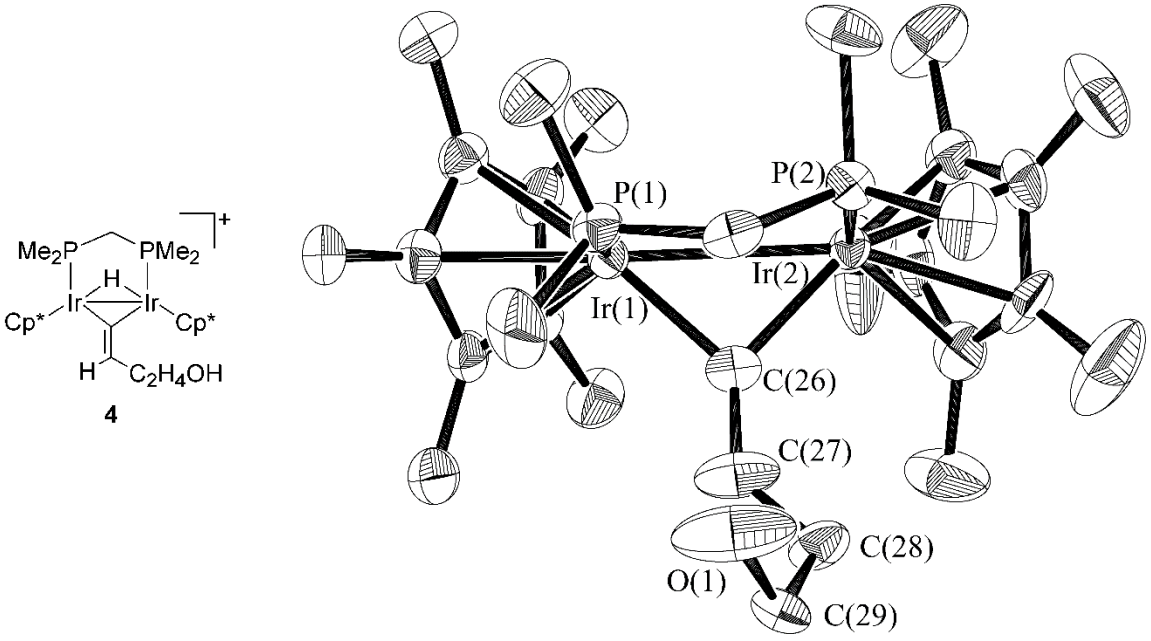

Figure S2. ORTEP Drawing of **4**. Hydrogen atoms are omitted for clarity. Two carbon atoms of -vinylidene group exhibited positional disorder (molecules A and B). Molecule A (61% occupancy) is shown here. Selected bond distances (Å) and angles (deg): Ir(1)−Ir(2) = 2.8381(3), Ir(1)−P(1) = 2.2512(19), Ir(2)−P(2) = 2.2378(19), Ir(1)−C(26) = 2.022(8), Ir(2) −C(26) = 2.029(5),C(26)−C(27) = 1.337(13), Ir(2)−Ir(1)−P(1) = 93.83(4), Ir(1)−Ir(2)−P(2) = 89.94(4), Ir(2)−Ir(1)−C(26) = 45.62(16), Ir(1)−Ir(2)−C(26) = 45.4(2), Ir(1)−C(26)−Ir(2) = 88.9(3), Ir(1)−C(26)−C(27) = 135.2(5), Ir(2)−C(26)−C(27) = 135.8(6).

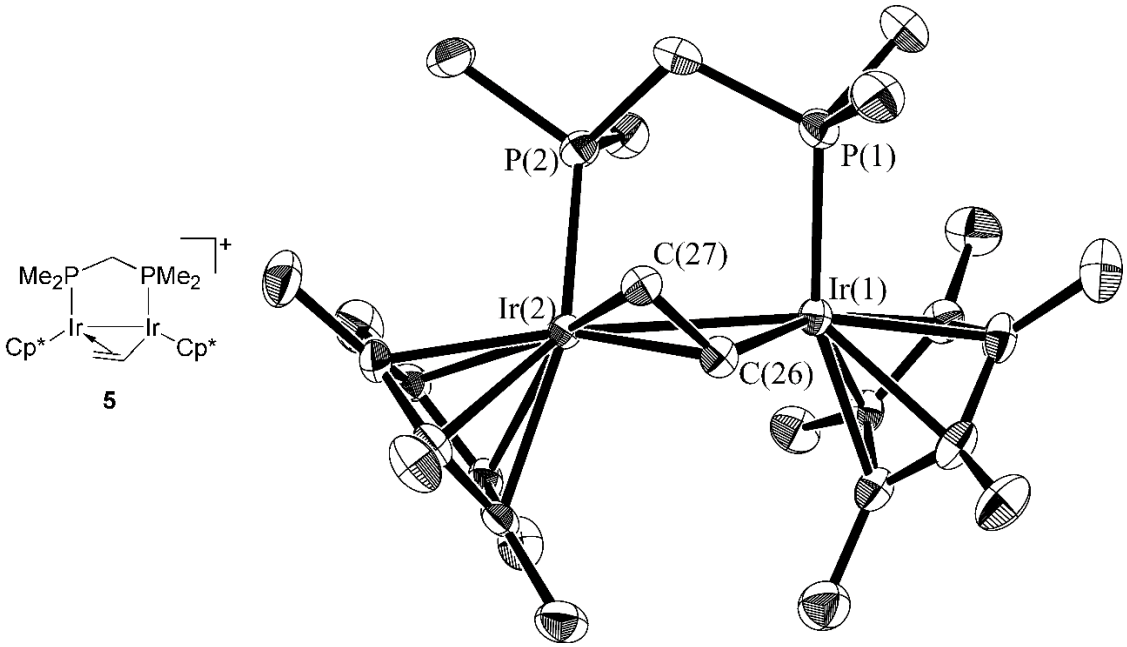

Figure S3. ORTEP Drawing of **5**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ir(1)−Ir(2) = 2.9397(2), Ir(1)−P(1) = 2.2522(12), Ir(2)−P(2) = 2.2567(11), Ir(1)−C(26) = 1.991(3), Ir(2) −C(26) = 2.147(4), Ir(2)−C(27) = 2.146(4), C(26)−C(27) = 1.408(6), Ir(2)−Ir(1)−P(1) = 92.29(3), Ir(1)−Ir(2)−P(2) = 79.77(3), Ir(2)−Ir(1)−C(26) = 46.91(13), Ir(1)−Ir(2)−C(26) = 42.63(10), Ir(1)−C(26)−Ir(2) = 90.46(17).

References

1 P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits, C. Smykalla, *PATTY*, Technical Report of the Crystallography Laboratory; University of Nijmegen: Nijmegen, The Netherlands, **1992**.

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3 (a) D. T. Cromer, G. T. Waber, *International Table for X-ray Crystallography*; Kynoch: Birmingham, U.K., **1974**; Vol. IV; (b) J. A. Ibers, W. C. Hamilton, *Acta Crystallogr*. **1964**, *17*, 781. (c) D. C. Creagh, W. J. McAuley in *International Tables for X-ray Crystallography*, ed: A. J. C. Wilson, Kluwer Academic Publishers: Boston, MA, **1992**; Vol. C; (d) D. C. Creagh, J. H. Hubbel in *International Tables for X-ray Crystallography*, ed: A. J. C. Wilson, Kluwer Academic Publishers: Boston, MA, **1992**; Vol. C.

4 *CrystalStructure3.8*, Crystal Structure Analysis Package; Rigaku and Rigaku/Molecular Structure Corp., **2000−2006.**

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