Reactions of Ir(acac)(cyclooctene)(PCy_3) with H_2, HC≡CR, $HSiR_3$, and $HSnPh_3$: The Acetylacetonato Ligand as a Stabilizer for Iridium(I), Iridium(III), and Iridium(V) Derivatives

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Received August 9, 1995[⊗]

The acetylacetonato complex Ir(acac)(cyclooctene)(PCy_3) (**1**) reacts with molecular hydrogen in the presence of 1 equiv of PCy_3 to give Ir(acac)H_2(PCy_3)$_2$ (**2**). The addition of 1 equiv of PhC≡CH to a benzene-d_6 solution of **1** causes the displacement of the coordinated olefin and the formation of Ir(acac)(η^2-PhC≡CH)(PCy_3) (**3**). The addition of hexane to this solution reverses the reaction and precipitates **1**. The treatment of **1** with 3 equiv of PhC≡CH affords Ir{κ^3-CH═C(Ph)CH[C(O)CH_3]$_2$}(C_2Ph)(CPh═CH_2)(PCy_3) (**4**), which is a result of the oxidative addition of the HC≡ bond of an alkyne, the insertion of a second alkyne into an Ir−C^3(acac) bond, and the subsequent insertion of a third alkyne into the Ir−H bond, previously formed. The structure of **4** was determined by an X-ray investigation. The coordination geometry around the iridium atom can be rationalized as a distorted octahedron with the bicyclic ligand occupying three coordination sites of a octahedral face. In the presence of PCy_3 the reaction of **1** and PhC≡CH leads to Ir(acac)H(C_2Ph)(PCy_3)$_2$ (**5**). Under the same conditions, CyC≡CH and Me_3SiC≡CH afford the corresponding hydrido−alkynyl derivatives Ir(acac)H-(C_2R)(PCy_3)$_2$ (R = Cy (**6**), Me_3Si (**7**)). The addition of silanes $HSiR_3$ to **1** gives Ir(acac)H-(SiR_3)(PCy_3) (SiR_3 = $SiEt_3$ (**8**), $SiPh_3$ (**9**), $SiHPh_2$ (**10**)). The structure of **8** was also determined by an X-ray analysis. The coordination geometry around the metallic center of **8** can be rationalized as a square pyramid with the triethylsilyl group located at the apex. In the presence of PCy_3, the reactions of **1** with silanes lead to Ir(acac)H(SiR_3)(PCy_3)$_2$ (SiR_3 = $SiEt_3$ (**11**), $SiHPh_2$ (**12**), SiH_2Ph (**13**)). Complex **1** also reacts with $HSnPh_3$. In the absence of PCy_3 the reaction product is Ir(acac)H($SnPh_3$)(PCy_3) (**14**), while in the presence of PCy_3 the six-coordinate derivative Ir(acac)H($SnPh_3$)(PCy_3)$_2$ (**15**) is obtained. Under atmospheric pressure of hydrogen, complex **8** is converted into the trihydrido−silyl−iridium(V) derivative Ir(acac)H_3($SiEt_3$)(PCy_3) (**32**). In solution, this complex is fluxional with values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ of 12.23 (± 0.76) kcal mol^{-1} and 1.45 (± 1.84) cal K^{-1} mol^{-1}, respectively. Complex **8** has also been found to be an active catalyst for the addition of $HSiEt_3$ to PhC≡CH. In all experiments, PhCH═CH_2, PhC≡C$SiEt_3$, *cis*-PhCH═CH($SiEt_3$), *trans*-PhCH═CH($SiEt_3$), and Ph($SiEt_3$)C═CH_2 were obtained. The major product in all cases is the thermodynamically less stable *cis*-PhCH═CH($SiEt_3$), resulting from the *anti*-addition of the silane to the alkyne. This product is selectively formed in approximately 70% yield.

Introduction

The catalytic properties of rhodium and iridium complexes containing P- and N-donors ligands have been intensely studied for many years.[1] However, the analogous chemistry with related O-donors has received less attention, even though metal crystallites and organometallic precursors supported on metal oxide surfaces are often catalytically active.[2]

One reason for the relative scarcity of studies on complexes containing Rh−O and Ir−O bonds is that such linkages are characteristically weak due to a mismatch of these hard basic ligands with the soft late transition metal centers.[3] However, the interest in how the properties of organometallic compounds change on moving from the more common P- and N-donor has led to an increase in the number of studies on these systems. As a result, species stabilized by O-donor ligands with interesting catalytic properties in reactions such as hydrogen transfer,[4] hydrosilylation,[5] and hydroboration[6] have been recently reported.

⊗ Abstract published in *Advance ACS Abstracts,* December 15, 1995.

(1) (a) Pignolet, L. H. *Homogeneous Catalysis with Metal Phosphine Complexes*; Plenum Press: New York, 1983. (b) Dickson, R. S. *Homogeneous Catalysis with compounds of Rhodium and Iridium*; Reidel Publishing Co.: Dordrecht, The Netherlands, 1985. (c) Chaloner, P. A.; Esteruelas, M. A.; Joó, F.; Oro, L. A. *Homogeneous Hydrogenation*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1994.

(2) (a) Ballard, D. G. H. *Adv. Catal.* **1973**, *23*, 263. (b) Yermarkov, Yu. Y.; Kuznetsov, B. N.; Zakharov, V. *Catalysis by Supported Complexes*, Elsevier: Amsterdam, 1981. (c) Schwartz, *J. Acc. Chem. Res.* **1985**, *18*, 302. (d) Gates, B. C.; Lamb, H. H. *J. Mol. Catal.* **1989**, *52*, 1.

(3) (a) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533. (b) Pearson, R. G. *J. Chem. Educ.* **1968**, *45*, 643.

(4) Uson, R.; Oro, L. A.; Ciriano, M. A.; Lahoz, F. J. *J. Organomet. Chem.* **1982**, *240*, 429.

(5) (a) Tanke, R. S.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1990**, 1056. (b) Tanke, R. S.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 7984. (c) Tanke, R. S.; Crabtree, R. H. *Organometallics* **1991**, *10*, 415.

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Table 1. ^{1}H NMR Data for Complexes 2, and 5−15[a]

complex	PCy_3	acac	X	Ir−H
2	2.21−1.26 (Cy)	1.30 (s, CH_3); 5.28 (s, CH)		−27.90 (t, J_{P-H} = 16 Hz)
5	2.32−1.12 (Cy)	1.86, 1.96 (both s, CH_3); 5.21 (s, CH)	7.69−6.95 (Ph)	−25.00 (t, J_{P-H} = 15 Hz)
6	2.25−1.14 (Cy)	1.75, 1.60 (both s, CH_3); 5.14 (s, CH)	2.25−1.14 (Cy)	−25.92 (t, J_{P-H} = 15 Hz)
7	2.25−1.20 (Cy)	1.65, 1.70 (both s, CH_3); 5.12 (s, CH)	1.20 (CH_3Si)	−29.50 (t, J_{P-H} = 15 Hz)
8	2.17−1.00 (Cy)	1.72(s, CH_3); 5.41(s, CH)	*b*; 0.86 (q, J_{H-H} = 7 Hz, CH_2)	−23.43 (d, J_{P-H} = 19 Hz)
9	2.20−0.95 (Cy)	1.78(s, CH_3); 5.21(s, CH)	8.06−7.16 (Ph)	−22.81 (d, J_{P-H} = 17 Hz)
10	2.25−1.22 (Cy)	1.73 (s, CH_3); 5.22 (s, CH)	8.19−7.12 (Ph); 7.75 (d, J_{P-H} = 7 Hz, Si−H)	−22.70 (d, J_{P-H} = 19 Hz)
11	2.25−0.89 (Cy)	1.89 (s, CH_3); 5.2 (s, CH)	1.35 (t, J_{H-H} = 7 Hz, CH_3); 1.25 (q, J_{H-H} = 7 Hz, CH_2)	−25.48 (t, J_{P-H} = 16 Hz)
12	2.20−0.85 (Cy)	1.76, 1.99 (both s, CH_3); 5.44 (s, CH)	8.08−7.21(Ph); 5.30 (t, J_{P-H} = 8 Hz, Si−H)	−25.44 (t, J_{P-H} = 16 Hz)
13	2.36−1.00 (Cy)	1.70, 1.92 (both s, CH_3); 5.35 (s, CH)	8.35−7.21(Ph); 4.22 (t, J_{P-H} = 5 Hz, Si−H_2)	−25.93 (t, J_{P-H} = 16 Hz)
14	2.07−0.90 (Cy)	1.61 (s, CH_3); 5.31 (s, CH)	7.92−7.12 (Ph)	−24.40 (d[c], J_{P-H} = 17 Hz)
15	2.12−1.11 (Cy)	1.61, 1.89 (both s, CH_3); 5.46 (s, CH)	8.05−7.12 (Ph)	−27.13 (t, J_{P-H} = 16 Hz)

[a] δ in ppm. Solvents: benzene-d_6 (**2**, **8**−**15**), chloroform-d_1 (**5**−**7**). Abbreviations used: s = singlet, d = doublet, t = triplet, q = quartet. [b] The CH_3 resonance is masked by the cyclohexyl signals. [c] With tin satellites, J_{Sn-H} = 88 Hz.

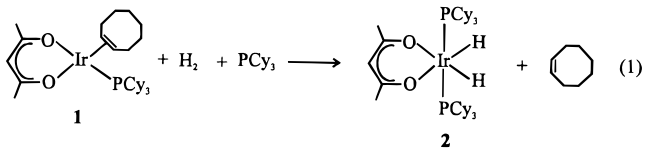
The design of a new catalyst requires a basic knowledge of the principal components of the catalytic cycles. In this respect, the oxidative additions of molecular hydrogen, terminal alkynes, and group 14 element hydrido compounds to unsaturated transition metal centers are reactions of considerable interest in connection with important homogeneous catalytic processes, including hydrogenation of unsaturated organic substrates,[1c] oligomerization of alkynes,[7] hydrosilylation,[8] and hydrostannation[9] of olefins and alkynes.

We recently reported the synthesis of the acetylacetonato complex Ir(acac)(cyclooctene)(PCy_3), which reacts with acetylenedicarboxylic methyl ester to give Ir(acac)(η^2-$CH_3O_2CC{\equiv}CCO_2CH_3$)($PCy_3$). The reaction of this complex with H_2SiPh_2 leads to Ir(acac){C[CH-(OCH$_3$)OSiPh$_2$]=CHCO$_2$CH$_3$}(PCy_3), which is a result of a net transformation involving addition of one Si−H bond across the C=O and another across the alkyne triple bond.[10] As a continuation of our work in this field, we have now studied the reactivity of the acetylacetonato complex Ir(acac)(cyclooctene)(PCy_3) toward molecular hydrogen, terminal alkynes, and group 14 element hydrido compounds.

In this paper we report the results of this study, the X-ray structure of the hydrido−silyl complex Ir(acac)H-($SiEt_3$)(PCy_3) and its catalytic activity in the hydrosilylation of phenylacetylene. In addition, the synthesis and X-ray structure of the unusual complex Ir{κ^3-CH=C(Ph)CH[C(O)CH$_3$]$_2$}(C$_2$Ph)(CPh=CH$_2$)(PCy_3) are also reported.

Results and Discussion

1. Reaction of Ir(acac)(cyclooctene)(PCy_3) with Molecular Hydrogen. On treatment with PCy_3, the bis(cyclooctene)iridium(I) complex Ir(acac)(cyclooctene)$_2$ affords the phosphine derivative Ir(acac)(cyclooctene)-(PCy_3) (**1**). The reaction proceeds at room temperature and does not lead to the displacement of the second olefin ligand, even in the presence of excess PCy_3.[10] Complex **1** is a yellow air-sensitive solid, which is stable under argon and hydrogen atmospheres in the solid state and in benzene-d_6 solution. While complex **1** does not react with PCy_3 or molecular hydrogen individually, the dihydrido compound Ir(acac)H_2(PCy_3)$_2$ (**2**) is easily formed by passing a slow stream of hydrogen through a solution of **1** in the presence of 1 equiv of PCy_3 (eq 1). Interestingly, under these conditions the cyclooctene olefin is not hydrogenated. A similar behavior has been observed for the ethylene derivative Ir(acac)(C_2H_4)(P^i-Pr_3).[11]



1 **2** (1)

Complex **2** was isolated as an air-stable powder in 89% yield and characterized by elemental analysis, IR, and ^{1}H and ^{31}P{^{1}H} NMR spectroscopies. In agreement with the *cis* dispositions of the hydrido ligands, the IR spectrum in Nujol shows two strong absorptions at 2240 and 2175 cm^{-1}. while in the ^{1}H NMR spectrum these ligands appear at −27.80 ppm as a triplet with a P−H coupling constant of 16 Hz (Table 1). The ^{31}P{^{1}H} NMR spectrum contains a singlet at 15.8 ppm, indicating that the phosphine ligands are equivalent and mutually trans disposed. Under off-resonance conditions, the singlet is split into a triplet due to the P−H coupling.

2. Reactions of Ir(acac)(cyclooctene)(PCy_3) with Phenylacetylene. The ^{31}P{^{1}H} NMR spectrum of **1** in benzene-d_6 shows a singlet at 1.4 ppm.[10] The addition of ca. 1 equiv of phenylacetylene to this solution causes the singlet to shift to 7.5 ppm. In the ^{1}H NMR spectrum, the most noticeable resonances of the new solution are the corresponding olefinic protons of the free cyclooctene olefin at 5.56 ppm and three singlets at 4.10 (HC≡), 1.90 (CH_3), and 1.50 (CH_3) ppm, with 1:3:3 intensity ratio, which are consistent with the formation of the π-alkyne derivative Ir(acac)(η^2-PhC≡CH)(PCy_3) (**3**) according to eq 2. Attempts to

(6) Westcott, S. A.; Blom, H. P.; Marder, T. B.; Baker, R. T. *J. Am. Chem. Soc.* **1992**, *114*, 8863.

(7) (a) Schäfer, M.; Mahr, N.; Wolf, J.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1315. (b) Bianchini, C.; Caulton, K. G.; Chardon, C.; Doublet, M.; Eisenstein, O.; Jackson, S. A.; Johnson, T. J.; Meli, A.; Peruzzini, M.; Streib, W. E.; Vacca, A.; Vizza, F. *Organometallics* **1994**, *13*, 2010. (c) Werner, H.; Schäfer, M.; Wolf, J.; Peters, K.; von Schnering, H. G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 191.

(8) (a) Ojima, I. *The Chemistry of Organic Silicom Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 25, p 1479. (b) Marciniec, B.; Gulinsky, J.; Urbaniak, W.; Kornetka, Z. W. *Comprehensive Handbook on Hydrosililation*; Marciniec, B., Ed.; Pergamon: Oxford, U.K., 1992; p 758. (c) Marciniec, B.; Gulinsky, J. *J. Organomet. Chem.* **1993**, *446*, 15.

(9) (a) Kikukawa, K.; Umekawa, H.; Wada, F.; Matsuda, T. *Chem. Lett.* **1988**, 881. (b) Esteruelas, M. A.; Lahoz, F. J.; Oliván, M.; Oñate, E.; Oro, L. A. *Organometallics* **1995**, *14*, 3486.

(10) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Rodríguez, L. *Organometallics* **1995**, *14*, 263.

(11) Papenfuhs, B.; Mahr, N.; Werner, H. *Organometallics* **1993**, *12*, 4244.

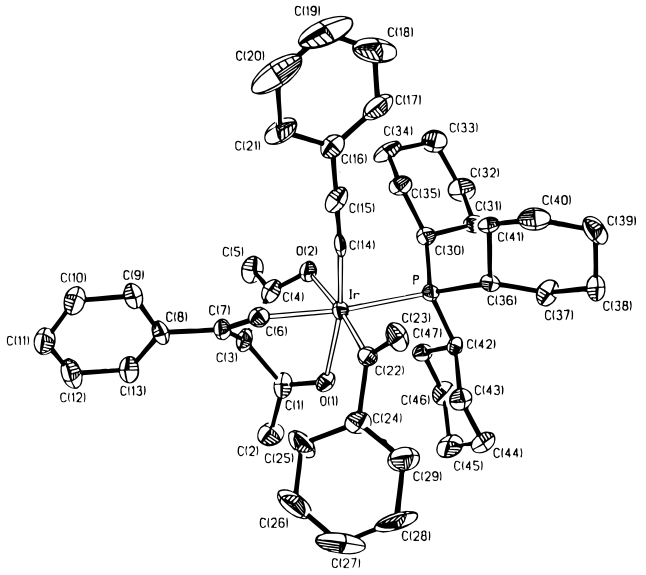
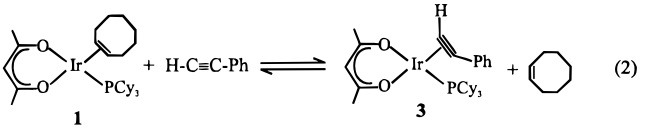
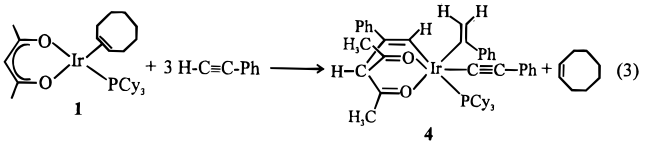


Figure 1. Molecular structure diagram of the complex Ir{κ^3-CH=C(Ph)CH[C(O)CH_3]$_2$}(C_2Ph)(CPh=CH_2)(PCy_3) (**4**).

isolate **3** remained unsuccessful. Thus, the addition of hexane to the benzene-d_6 solution of **3** and cyclooctene reverses the reaction and precipitates **1**.



Treatment of **1** with ca. 3 equiv of phenylacetylene in benzene leads, after 1 h at room temperature, to an orange solution from which the compound Ir{κ^3-CH=C(Ph)CH[C(O)CH_3]$_2$}(C_2Ph)(CPh=CH_2)(PCy_3) (**4**) (eq 3) was separated as an orange crystalline solid in 73% yield, by addition of hexane.



Complex **4** was fully characterized by elemental analysis, IR and ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectroscopic data, and X-ray diffraction. A drawing of the molecular structure is shown in Figure 1. Selected bond distances and angles are listed in Table 2.

The single crystal X-ray diffraction analysis of **4** reveals the presence of the unusual κ^3-CH=C(Ph)CH[C(O)CH_3]$_2$ ligand, which is a result of the 1,4-addition of a phenylacetylene across the β-ketoenolate−iridium ring. We note that examples illustrating the 1,4-addition of activate internal alkynes across the β-ketoenolato−iridium and −rhodium rings have been previously described.[12] However, nothing is known about this reaction with nonactivating terminal alkynes. The bicyclic system occupies three coordination sites to form a face of the octahedral environment around the iridium atom. The C(6) carbon atom is disposed *trans* to the tricyclohexylphosphine ligand (P−Ir−C(6) = 171.6(3)°), while the O(1) and O(2) oxygen atoms are situated *trans* to the alkynyl (O(1)−Ir−C(14) = 170.1(3)°) and alkenyl (O(2)−Ir−C(22) = 173.6(4)°) groups, respectively.

Table 2. Bond Distances (Å) and Angles (deg) for the Compound Ir{κ^3-CH=C(Ph)CH[C(O)CH_3]$_2$-(C_2Ph)[CPh=CH_2](PCy_3) (4)

Ir−P	2.423(2)	C(3)−C(7)	1.545(15)
Ir−O(1)	2.204(8)	C(4)−C(5)	1.493(15)
Ir−O(2)	2.222(8)	O(2)−C(4)	1.219(14)
Ir−C(6)	2.030(9)	C(6)−C(7)	1.318(15)
Ir−C(14)	1.897(11)	C(7)−C(8)	1.495(14)
Ir−C(22)	2.017(10)	C(22)−C(23)	1.371(15)
O(1)−C(1)	1.243(12)	C(22)−C(24)	1.542(16)
C(1)−C(2)	1.445(17)	C(14)−C(15)	1.268(16)
C(1)−C(3)	1.523(14)	C(15)−C(16)	1.408(17)
C(3)−C(4)	1.528(18)		
P−Ir−O(1)	95.9(2)	C(2)−C(1)−C(3)	121(1)
P−Ir−O(2)	88.3(2)	C(1)−C(3)−C(4)	109.2(8)
P−Ir−C(6)	171.6(3)	C(1)−C(3)−C(7)	110.7(8)
P−Ir−C(14)	93.6(3)	C(4)−C(3)−C(7)	119.2(9)
P−Ir−C(22)	94.9(3)	C(3)−C(4)−C(5)	118(1)
O(1)−Ir−O(2)	81.1(3)	O(2)−C(4)−C(3)	120.0(9)
O(1)−Ir−C(6)	85.0(3)	O(2)−C(4)−C(5)	122(1)
O(1)−Ir−C(14)	170.1(3)	Ir−O(2)−C(4)	119.2(8)
O(1)−Ir−C(22)	93.0(4)	Ir−C(6)−C(7)	122.5(8)
O(2)−Ir−C(6)	83.7(3)	C(6)−C(7)−C(8)	126(1)
O(2)−Ir−C(14)	96.3(4)	C(3)−C(7)−C(6)	116.9(9)
O(2)−Ir−C(22)	173.6(4)	C(3)−C(7)−C(8)	117.2(9)
C(6)−Ir−C(14)	85.2(4)	Ir−C(14)−C(15)	176.4(9)
C(6)−Ir−C(22)	93.4(4)	C(14)−C(15)−C(16)	179(1)
C(14)−Ir−C(22)	89.1(4)	Ir−C(22)−C(23)	126.5(9)
Ir−O(1)−C(1)	119.7(6)	Ir−C(22)−C(24)	119.3(7)
O(1)−C(1)−C(2)	120(1)	C(23)−C(22)−C(24)	114.2(9)
O(1)−C(1)−C(3)	119(1)		

The geometry of the κ^3-CH=C(Ph)CH[C(O)CH_3]$_2$ ligand is similar to that previously reported for κ^3-C(CF_3)=C(CF_3)CH[C(O)CH_3]$_2$.[12] As expected the C(1)−O(1) (1.243(12) Å) and C(4)−O(2) (1.219(14) Å) bond lengths are about 0.8 Å shorter than those observed in delocalized acetylacetonato ligands coordinated to iridium(III) fragments (mean value 2.082 Å),[13] while the C(1)−C(3) (1.523(14) Å) and C(3)−C(4) (1.528(18) Å) distances are about 0.15 Å longer (mean 1.383 Å).[13] The C(6)−C(7) (1.318(15) Å) and C(3)−C(7) (1.545(15) Å) bond lengths compare well with the values of carbon−carbon double bonds (1.32 Å) and carbon−carbon single bonds (1.53 Å),[14] respectively. The Ir−O(1) (2.204(8) Å) and Ir−O(2) (2.222(8) Å) distances are statistically identical and significatively longer than the mean of the Ir−O distances previously reported (2.088 Å).[13] Ir−C(6) (2.030(9) Å) and Ir−C(22) (2.017(10) Å) are also statistically identical and shorter than the Ir−C bond lengths found in the alkenyliridium(III) complexes IrH(CH=CH_2)Cl(CO)(P^iPr_3)$_2$ (2.059(6) Å)[15] and IrH(CH=CH_2)(η^5-C_5Me_5)(PMe_3) (2.054(4) Å).[16] However, they are almost identical with those of the complexes [IrH{C(COOCH_3)=CH_2}(Hpz)(PPh_3)$_2$]BF_4 (Hpz = pyrazole; 2.02(2) Å)[17] and IrH(acac)(CH=CH_2)(P^iPr_3)$_2$ (2.02(1) Å).[11] The Ir−C(14) length (1.897(11) Å) is consistent with a single

(12) (a) Russell, D. R.; Tucker, P. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1749. (b) Barlow, J. H.; Clark, G. R.; Curl, M. G.; Howden, M. E.; Kemmitt, R. D. W.; Russell, D. R. *J. Organomet. Chem.* **1978**, *144*, C47. (c) Jarvis, A. C.; Kemmitt, R. D. W.; Russell, D. R.; Tucker, P. A. *J. Organomet. Chem.* **1978**, *159*, 341.

(13) Allen, F. H.; Davies, J. E.; Galloy, J. J.; Johnson, O.; Kennard, O.; Macrae, C. F.; Mitchell, E. M.; Mitchell, G. F.; Smith, J. M.; Watson, D. G. *J. Chem. Info. Comput. Sci.* **1991**, *31*, 187.

(14) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, G.; Taylor, R. *J. Chem. Soc., Perkin Trans.* **1987**, S1.

(15) Schulz, M.; Werner, H. *Organometallics* **1992**, *11*, 2790.

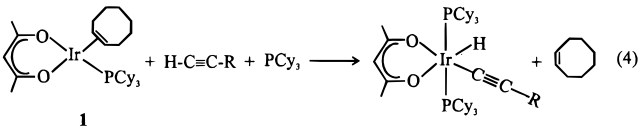
(16) (a) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 5481. (b) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 5732.

(17) Esteruelas, M. A.; García, M. P.; Martín, M.; Nürnberg, O.; Oro, L. A.; Werner, H. *J. Organomet. Chem.* **1994**, *466*, 247.

bond from Ir(III) to a C(sp) atom and indicates a low degree of metal-to-ligand back-bonding.[18] The C(14)−C(15) bond length and C(14)−C(15)−C(16) angle are 1.268(16) Å and 179(1)°, respectively; a slight bending in the Ir−C(14)-C(15) moiety is present (Ir−C(14)−C(15) = 176.4(9)°); similar values have been found for related complexes containing terminal alkynyl groups.[19]

In agreement with the structure shown in Figure 1, the $^{13}C\{^1H\}$ NMR spectrum of **4** in chloroform-*d* shows four doublets at 166.93 (J_{P-C} = 92 Hz), 141.71 (J_{P-C} = 6 Hz), 125.81 (J_{P-C} = 4 Hz), and 119.99 (J_{P-C} = 4 Hz) ppm and two singlets at 153.92 and 131.13 ppm, which were assigned to the carbon atoms C(6), C(7), C(14), C(22), C(23) and C(15), respectively. In the ^1H NMR spectrum the most noticeable resonances are a singlet at 9.15 ppm, assigned to Ir−CH= proton and two virtual triplets at 5.69 and 5.19 ppm, with H−H and P−H coupling constants of 3 Hz, which were assigned to the $=CH_2$ protons. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at −2.5 ppm.

Similarly to the reaction shown in eq 1, complex **1** reacts with phenylacetylene in the presence of 1 equiv of tricyclohexylphosphine to afford the hydrido−alkynyl complex Ir(acac)H(C_2Ph)(PCy_3)$_2$ (**5**). Under the same conditions the treatment of **1** with cyclohexylacetylene and (trimethylsilyl)acetylene leads to the corresponding hydrido−alkynyl derivatives Ir(acac)H(C_2R)(PCy_3)$_2$ (R = Cy (**6**), $SiMe_3$ (**7**)) (eq 4).

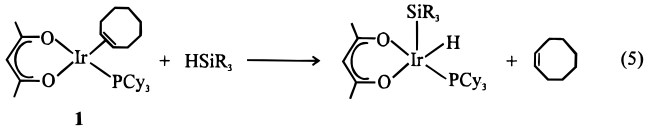


1

R= Ph (**5**), Cy (**6**), $SiMe_3$ (**7**)

Complexes **5**−**7** were isolated as white or pale yellow solids in about 50% yield. In the IR spectra in Nujol the most noticeable absorptions are two bands between 2300 and 2000 cm^{-1}, which were assigned to the ν(Ir−H) and ν(C≡C) vibrations. The presence of an alkynyl ligand is also supported by the $^{13}C\{^1H\}$ NMR spectra. The C_α carbon atoms appear at about 128 ppm as triplets with P−C coupling constants between 8 and 13 Hz, while the C_β carbon atoms display singlets at about 130 ppm. In the ^1H NMR spectra (Table 1) the hydrido ligands appear between −25 and −29 ppm, as triplets with P−H coupling constants of 15 Hz. The presence of only one hydrido ligand in these compounds was inferred from the $^{31}P\{^1H\}$ NMR spectra, which contain, in agreement with the mutually *trans* disposition of the phosphine ligands, singlets at about 15 ppm that under off-resonance conditions due to P−H coupling are split into doublets.

3. Reactions of Ir(acac)(cyclooctene)(PCy_3) with $HSiR_3$. The addition of ca. 1 equiv of $HSiEt_3$, $HSiPh_3$, and H_2SiPh_2 to solutions of **1** in benzene leads after 30 min to the corresponding five-coordinate hydrido−silyl complexes Ir(acac)H(SiR_3)(PCy_3) (SiR_3 = $SiEt_3$ (**8**), $SiPh_3$ (**9**), $SiHPh_2$ (**10**)), according to eq 5. Five-coordinate hydrido−silyl−iridium(III) compounds are rare, as far as we know, the derivatives of this type previously



1

SiR_3= $SiEt_3$ (**8**), $SiPh_3$ (**9**), $SiHPh_2$ (**10**)

reported have the formula Ir$HX(SiR_3)(PR_3)_2$, and they have been prepared by oxidative addition of silanes to IrX(olefin)$(PR_3)_2$ (X = Cl, Br)[20,21] and by reaction of $IrH_5(PR_3)_2$ with chlorosilanes in the presence of olefins.[22]

Complex **8** was isolated as a yellow crystalline solid in 93% yield and characterized by elemental analysis, IR and ^1H (Table 1) and $^{31}P\{^1H\}$ spectroscopic data, and X-ray diffraction. A drawing of the molecular structure is presented in Figure 2. Selected bond distances and angles are listed in Table 3.

The geometry can be rationalized as a square pyramid with the triethylsilyl group located at the apex. The four atoms O(1), O(2), P, and H(1) forming the base are approximately coplanar, whereas the iridium atom is located 0.2394(4) Å above this plane toward the apical position. We note that the molecular structures of the five-coordinate complexes IrHCl(Si^iPr_2OH)(PEt_3)$_2$[21] and IrHCl($SiCl_2CH_3$)(P^iPr_3)$_2$[22] have been previously determined by X-ray diffraction. In contrast to **8**, they show trigonal bipyramidal arrangements of the ligands around the metallic center.

The Ir−Si distance of 2.307(1) Å is significantly shorter than those determined previously for the six-coordinate iridium(III) complexes $IrH_2(SiEt_3)$(COD)(AsPh$_3$) (2.414(2) Å),[23] $IrH_2(SiMe_2Ph)(CO)\{P(p\text{-}tol)_3\}_2$ (2.414(2) Å),[24] IrH($SiMe_2Cl$)(CO)(dppe) (dppe = 1,2-bis(diphenylphosphino)ethane) (2.396(2) Å), IrH($SiEtF_2$)$_2$(CO)(dppe) (2.360(10) Å),[25] and Ir$H\{Si(C_6H_4)Ph_2\}(PMe_3)_3$ (2.404(3) Å).[26] However, it is similar to that found in the pentacoordinated complex IrHCl(Si^iPr_2OH)(PEt_3)$_2$ (2.313(6) Å)[21] and in the six-coordinate complex $IrCl_2(SiMeCl_2)(PMe_3)_3$ (2.299(5) Å)[27] and longer that those found in the other five-coordinate derivatives IrHCl($SiMe_2Cl_2$)(P^iPr_3)$_2$ (2.235(5) Å)[22] and Ir(acac)$\{C[CH(OCH_3)OSiPh_2]{=}CHCO_2CH_3\}(PCy_3)$ (2.264(2) Å).[10]

It should be also mentioned that the Ir−O(2) bond distance (2.073(3) Å; O *trans* to P) is significantly shorter than the Ir−O(1) bond distance (2.121(2) Å; O *trans* to H), possibly due to the different *trans* influences of the phosphine and hydrido ligands. The O(1)−C(1) (1.298(5) Å), C(1)−C(3) (1.382(6) Å), C(3)−C(4) (1.394(6) Å), and C(4)−O(2) (1.267(5) Å) distances compare well with those found in the delocalized acetylacetonato ligand coordinated to other Ir(III) fragments.[11,13] The

(18) Bruce, M. I.; Hambley, T. W.; Snow, N. R.; Swincer, A. G. *J. Organomet. Chem.* **1982**, *235*, 105.
(19) (a) Nast, R. *Coord. Chem. Rev.* **1982**, *47*, 89. (b) Fernández, M. J.; Esteruelas, M. A.; Covarrubias, M.; Oro, L. A.; Apreda, M. C.; Foces-Foces, C.; Cano, F. H. *Organometallics* **1989**, *8*, 1158.
(20) Blackburn, S. N.; Haszeldine, R. N.; Parish, R. V.; Setchfield, J. H. *J. Chem. Res. (S)* **1980**, 170.
(21) Goikhman, R.; Aizenberg, M.; Kraatz, H. B.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 5865.
(22) Yamashita, H.; Kawamoto, A. M.; Tanaka, M.; Goto, M. *Chem. Lett.* **1990**, 2107.
(23) Fernández, M. J.; Esteruelas, M. A.; Oro, L. A.; Apreda, M. C.; Foces-Foces, C.; Cano, F. H. *Organometallics* **1987**, *6*, 1751.
(24) Rappoli, B. J.; Janik, T. C.; Churchill, M. R.; Thompson, J. S.; Atwood, J. D. *Organometallics* **1988**, *7*, 1939.
(25) Hays, M. K.; Eisenberg, R. *Inorg. Chem.* **1991**, *30*, 2623.
(26) Aizenberg, N.; Milstein, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 317.
(27) Zlota, A. A.; Frolow, F.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1989**, 1826.

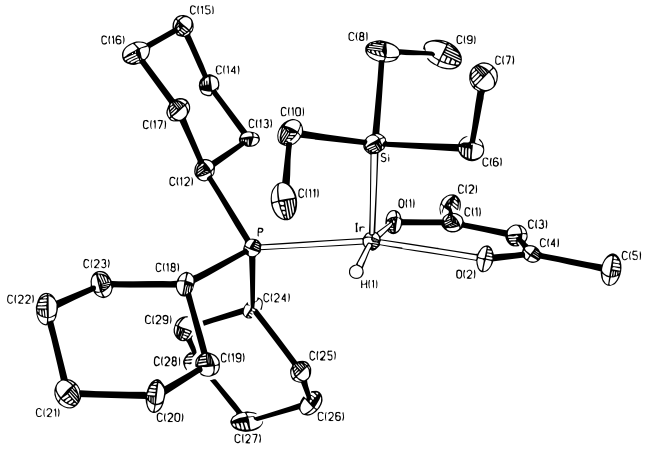


Figure 2. Molecular structure diagram of the complex Ir(acac)H($SiEt_3$)(PCy_3) (**8**).

Table 3. Bond Distances (Å) and Angles (deg) for the Compound Ir(acac)H($SiEt_3$)(PCy_3) (8)

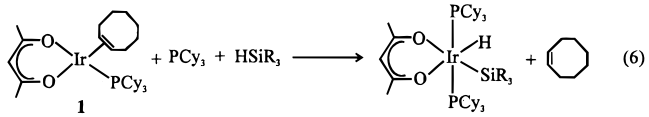
Ir−P	2.235(1)	C(1)−C(2)	1.509(6)
Ir−Si	2.307(1)	C(1)−C(3)	1.382(6)
Ir−O(1)	2.121(2)	C(3)−C(4)	1.394(6)
Ir−O(2)	2.073(3)	O(2)−C(4)	1.267(5)
Ir−H(1)	1.44(4)	C(4)−C(5)	1.518(6)
O(1)−C(1)	1.298(5)		
P−Ir−Si	101.19(4)	Ir−O(1)−C(1)	125.7(2)
P−Ir−O(1)	91.38(8)	O(1)−C(1)−C(2)	114.8(3)
P−Ir−O(2)	167.19(8)	O(1)−C(1)−C(3)	126.2(4)
P−Ir−H(1)	90(1)	C(2)−C(1)−C(3)	119.0(4)
Si−Ir−O(1)	122.52(8)	C(1)−C(3)−C(4)	126.5(4)
Si−Ir−O(2)	90.04(8)	C(3)−C(4)−C(5)	119.7(4)
Si−Ir−H(1)	69(1)	O(2)−C(4)−C(3)	126.5(4)
O(1)−Ir−O(2)	87.7(1)	O(2)−C(4)−C(5)	113.8(4)
O(1)−Ir−H(1)	168(1)	Ir−O(2)−C(4)	127.4(3)
O(2)−Ir−H(1)	88(1)		

Ir−P (2.235(1) Å) bond length is also in the expected range and deserves no further comment.

The ^1H and $^{31}P\{^1H\}$ spectra of **8** are temperature invariant, suggesting that although **8** is a five-coordinate derivative, it has a rigid structure in solution. In agreement with the structure shown in Figure 2, the hydrido ligand appears in the ^1H NMR spectrum at −23.47 ppm as a doublet with a P−H coupling of 19 Hz. Similar chemical shifts have been observed for the hydrido ligands of the acetato complexes $IrH_2\{\eta^2\text{-}O_2CR\}(PPh_3)_2$, where the hydridos also are disposed *trans* to an O-donor ligand.[28] As the ^1H NMR spectrum of **8**, the ^1H NMR spectra of **9** and **10** contain doublets at −22.81 (**9**) and −22.70 (**10**) ppm with P−H coupling constants of 17 and 19 Hz, respectively. The $^{31}P\{^1H\}$ NMR spectra of the three compounds show singlets between 6 and 12 ppm, which under off-resonance conditions due to P−H coupling are split into doublets, in accordance with the presence of only one hydrido ligand in these compounds.

The complexes **8** and **10** do not react with tricyclohexylphosphine. However, the addition of ca. 1 equiv of $HSiEt_3$, H_2SiPh_2, and H_3SiPh to toluene solutions of **1** in the presence of 1 equiv of tricyclohexylphosphine affords the six-coordinate hydrido−silyl derivatives Ir(acac)H(SiR_3)(PCy_3)$_2$ (SiR_3 = $SiEt_3$ (**11**), $SiHPh_2$ (**12**), SiH_2Ph (**13**)), which were isolated as white solids in 40−60% yield (eq 6).

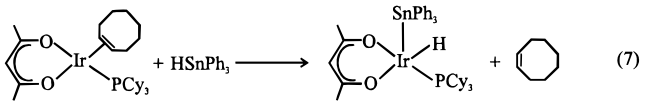
(28) Esteruelas, M. A.; García, M. P.; Lahoz, F. J.; Martín, M.; Modrego, J.; Oñate, E.; Oro, L. A. *Inorg. Chem.* **1994**, *33*, 3473.



SiR_3 = $SiEt_3$ (**11**), $SiHPh_2$ (**12**), SiH_2Ph (**13**)

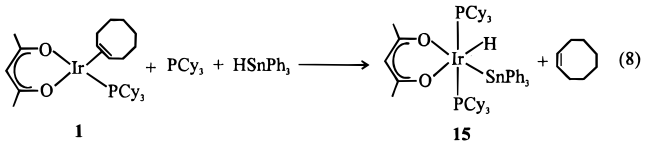
The most noticeable absorptions in the IR spectra in Nujol of **11**−**13** are those corresponding to the ν(Ir−H) vibrations, which appear between 2240 and 2210 cm^{-1}. In the ^1H NMR spectra (Table 1) the hydrido ligands display triplets at about −25.5 ppm, with P−H coupling constants of 16 Hz. The $^{31}P\{^1H\}$ NMR spectra show singlets between 9.4 and 15.9 ppm, which under off-resonance conditions due to P−H coupling are split into doublets.

4. Reactions of Ir(acac)(cyclooctene)(PCy_3) with $HSnPh_3$. The addition of ca. 1 equiv of $HSnPh_3$ to a benzene-d_6 solution of **1** leads after 5 min to the five-coordinate hydrido−stannyl complex Ir(acac)H($SnPh_3$)(PCy_3) (**14**), according to eq 7.



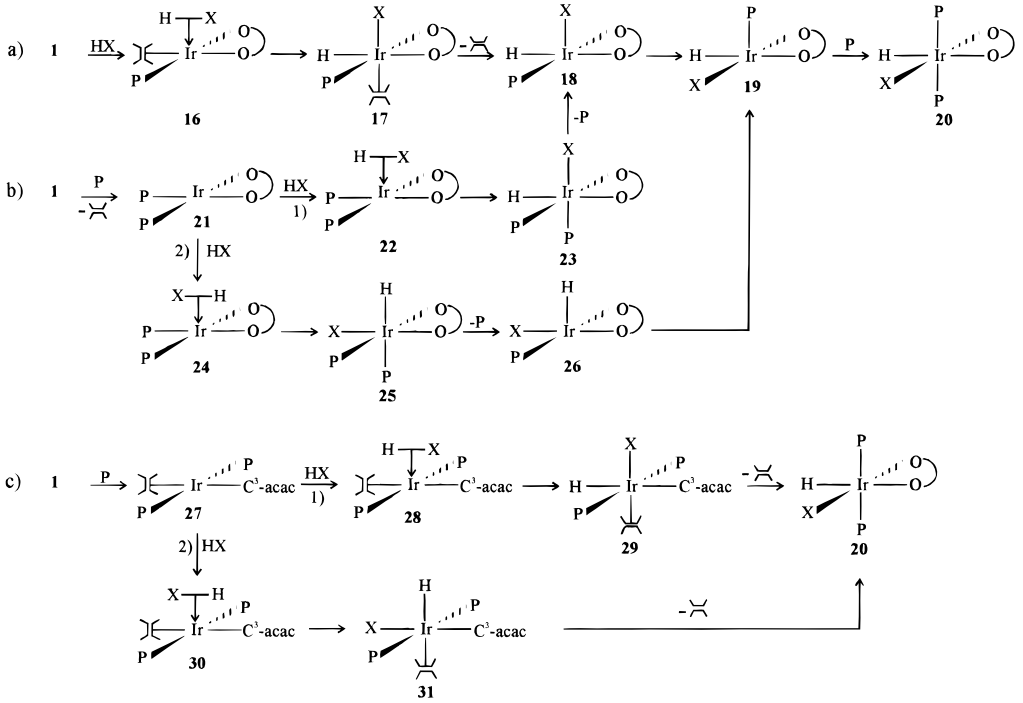
The ^1H and $^{31}P\{^1H\}$ NMR spectra of **14** strongly support the structure shown in eq 7. The ^1H NMR spectrum (Table 1) contains in the high-field region a doublet at −24.44 ppm, with a P−H coupling constant of 17 Hz. The satellites due to the Sn isotopes are also observed near to this resonance. The value of the Sn−H coupling constant, 88 Hz, is in agreement with the *cis* situation of the triphenylstannyl group and the hydrido ligand. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 7.6 ppm, along with the satellites corresponding to the tin active isotopes. The value of the P−Sn coupling constant, 44 Hz, also agrees well with the mutually *cis* disposition of the $SnPh_3$ and PCy_3 groups. Under off-resonance conditions due to P−H coupling the singlet is split into a doublet.

Similary to **8**, complex **14** does not react with tricyclohexylphosphine. However, the addition of ca. 1 equiv of $HSnPh_3$ to a toluene solution of **1** in the presence of 1 equiv of phosphine leads to the six-coordinate hydrido−stannyl derivative Ir(acac)H($SnPh_3$)(PCy_3)$_2$ (**15**), according to eq 8.



Complex **15** was isolated as a pale yellow solid in 61% yield. In the IR spectrum in Nujol, the most noticeable absorption is that corresponding to the ν(Ir−H) vibration, which appears at 2225 cm^{-1}. In the ^1H NMR spectrum (Table 1) the hydrido ligand gives rise to a triplet at −27.13 ppm with a P−H coupling constant of 16 Hz. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 7.6 ppm, along with the satellites due to the ^{117}Sn and ^{119}Sn isotopes. In agreement with the structure shown in eq 8, the value of the P−^{119}Sn coupling constant is 142 Hz, while the value the P−^{117}Sn coupling

Scheme 1



constant is 113 Hz. Under off-resonance conditions due to P−H coupling the singlet is split into a doublet.

5. Comments on the Formation of the Six-Coordinate Complexes Ir(acac)HX(PCy$_3$)$_2$. The oxidative addition of molecular hydrogen and group 14 element hydrido compounds to iridium(I) complexes is generally viewed as a concerted *cis* addition.[29] Furthermore, Johnson and Eisenberg[30] have proved that the addition of $HSiR_3$ to iridium(I) *cis*-phosphine complexes, IrX(CO)(dppe) (X = Br, CN), is a diasteroselective process with specific substrate orientation. We have recently observed that the oxidative addition of $HSnR_3$ to Ir(C_2Ph)(L_2)(PCy_3) (L_2 = 2 CO, tetrafluorobenzobarrelene (TFB)) is also a diasteroselective *cis* addition process with specific substrate orientation.[9b] According to this, Scheme 1 shows three different reaction pathways which allow the formation of **2**, **5**−**7**, **11**−**13**, and **15** to be rationalized. These compounds are formed by reaction of **1** with the substrate HX in the presence of 1 equiv of tricyclohexylphosphine (eqs 1, 4, 6, and 8). Therefore, the reactions could initially involve the interaction of **1** with the substrate HX (pathway **a**) or alternatively with the phosphine (pathways **b** and **c**).

According to pathway **a**, the oxidative addition of HX to **1** along the olefin−Ir−O(acac) axis yields a six-coordinate intermediate **17**, which by subsequent disociation of cyclooctene affords **18**, isolated for X = $SiEt_3$, $SiPh_3$, $SiHPh_2$, and $SnPh_3$. The isomerization of these five-coordinate derivatives followed by the coordination of the phosphine, which is present in the reaction, should lead to the reaction products. Hence, the formation of the compounds of the type Ir(acac)HX(PCy_3)$_2$ according to pathway **a** involves the initial formation of the derivatives **18** and its subsequent reaction with the phosphine ligand. This pathway can be totally ruled out. Since, we have previously mentioned that the derivatives **8**−**10** do not react with tricyclohexylphosphine.

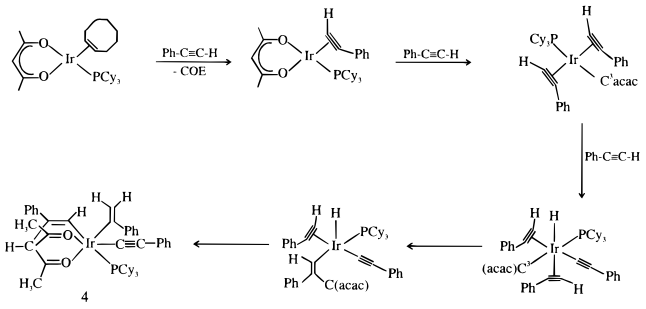
According to pathway **b**, the reactions shown in the eqs 1, 4, 6, and 8 involve the initial formation of the bis(phosphine) intermediate **21**. The oxidative addition of the substrate HX must initially lead to six-coordinate derivatives, containing the phosphine ligands mutually *cis* disposed. The isomerization of these intermediates could yield the reaction products. However, it should be noted that this isomerization occurs by disociation of phosphine and, therefore, via five-coordinate mono(phosphine) derivatives, which do not recoordinate phosphine. At first glance, one could think that the isomerization of **23** and/or **25** into the reactions product involves five-coordinate intermediates containing the acetylacetonato ligand coordinated in an η^1-fashion. This does not seem likely due to the low tendency shown by the d^6 ions to afford unsaturated compounds containing η^1-chelate ligands. Furthermore, it should be noted that these five-coordinate intermediates should also be accesible from Ir(acac)HX(PCy_3)$_2$ by reaction with phosphine, which does not occur.

The d^8 ions show a higher tendency than the d^6 ions to afford unsaturated species. Thus, the addition of phosphine to the solutions of **1** could give the unsaturated square-planar intermediate **27** (pathway **c**) containing the acetylacetonato coordinate in a η^1-C^3-fashion. In iridium there is precedent for this reaction, as we have previously reported that the addition of N-donor ligands to Ir(acac)(diolefin) leads to the corresponding Ir(η^1-C^3-acac) derivatives.[31] The oxidative addition of the substrate HX along of the olefin−Ir−C^3-(acac) axis should give **29** or **31**. The subsequent η^1-C^3

(29) (a) Sommer, L. H.; Lyons, J. E.; Fujimoto, H. J. *J. Am. Chem. Soc.* **1969**, *91*, 7051. (b) Harrod, F. J.; Smith, C. A.; Thank, K. A. *J. Am. Chem. Soc.* **1972**, *94*, 8321. (c) Fawcett, J. P.; Harrod, J. F. *J. Organomet. Chem.* **1976**, *113*, 245. (d) Benett, M. A.; Charles, R.; Fraser, P. *J. Aust. J. Chem.* **1977**, *30*, 1201. (e) Johnson, C. E.; Fisher, B. J.; Eisenberg, R. *J. Am. Chem. Soc.* **1983**, *105*, 7772. (f) Johnson, C. E.; Eisenberg, R. *J. Am. Chem. Soc.* **1985**, *107*, 3148.

(30) Johnson, C. E.; Eisenberg, R. *J. Am. Chem. Soc.* **1985**, *107*, 6531.

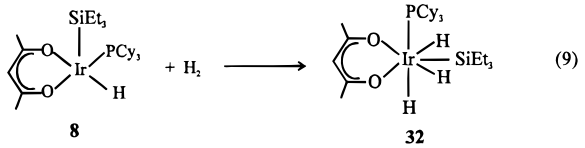
Scheme 2



→ η^2-*O*,*O*′ conversion of the acetylacetonato ligand together with the displacement of the olefin could afford the reactions products. The synthesis of complex **4** according to eq 3 is strong evidence in favor of pathway **c**. Scheme 2 shows a plausible reaction pathway for the formation of this compound, which involves the oxidative addition of the HC≡ bond of an alkyne, the insertion of a second alkyne into a Ir−η^1-C^3(acac) bond, and insertion of a third alkyne into a Ir−H bond. As far as we know, these three reactions sequential on the same metallic center have no precedent.

In addition, it should be mentioned the high stability of the six-coordinate derivatives **2**, **5**−**7**, **11**−**13**, and **15** toward the reductive elimination of HX can be related to the *cis* constraint imposed by the chelating acetylacetonato ligand and the fact that in a concerted reductive elimination the ligands *trans* to the leaving groups move into mutually *trans* positions in the resulting four-coordinate complex.[32]

6. Reaction of Ir(acac)H($SiEt_3$)(PCy_3) with Molecular Hydrogen. Under atmospheric pressure of hydrogen, complex **8** is converted into the trihydrido−silyl−iridium(V) derivative Ir(acac)H_3($SiEt_3$)(PCy_3) (**32**). Figure 3 shows the ^{1}H NMR spectrum of this compound, in the hydrido region, as a function of the temperature. At 295 K the spectrum contains a broad resonance at about −24 ppm, which is converted into the AM_2 part of an AM_2X spin system at 230 K. The position (δ_A = −3.64 and δ_M = −23.26) and the values of the coupling constants (J_{A-M} = 0, J_{A-X} = 119.0 and J_{M-X} = 19.9 Hz) strongly support the structure shown in eq 9.



The ^{31}P{^{1}H} NMR spectrum of **32** shows a singlet at 21.8 ppm which is temperature invariant, suggesting that the fluxional process only involves the relative positions of the hydrido ligands. Linear least-squares analysis of the Eyring plot for the kinetic data (Figure 4) provides values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ of 12.23(± 0.76) kcal mol^{-1} and −1.45(±1.84) cal K^{-1} mol^{-1}, respectively. The value of the entropy of activation, close to zero, is in agreement with an intramolecular process. Furthermore, it should be mentioned that the reaction shown in the eq 9 is completely reversible under vacuum at room temperature. This suggests that the exchange process could take place by dihydrogen intermediates. A plausible mechanism for fluxionality which accounts for the observations is shown in Scheme 3.

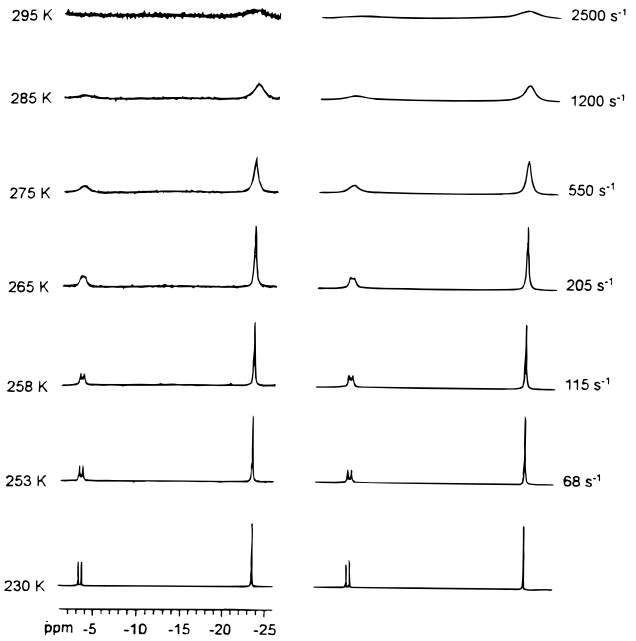


Figure 3. Experimental (left) and computed (right) high-field region of the variable-temperature ^{1}H NMR spectra of **32** (toluene-d_8, 300 MHz).

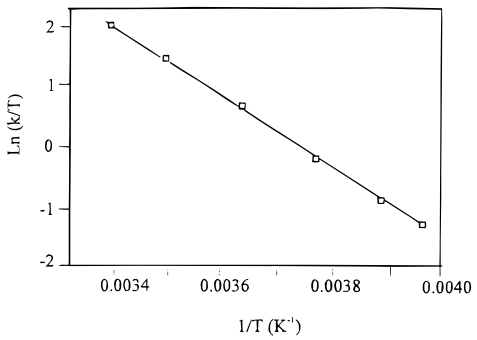


Figure 4. Eyring plot of the dynamic process of **32** as deduced from line shape analysis of the variable-temperature ^{1}H NMR spectra.

Trihydrido−silyl complexes are rare;[33] indeed **32** is the only example with an O-donor ligand. Apart from **32**, the only other trihydrido−silyl complexes examples are the derivatives Ir(η^5-C_5Me_5)H_3($SiMe_3$)[34] and IrH_3(η^2-$R_2SiXSiR_2$)(PPh_3)$_2$ (X = C_6H_4, R = Me; X = O, R = ^{i}Pr).[35] Complex **32** is also significant because it proves that the acetylacetonato ligand not only stabilizes Ir(I) and Ir(III) but also Ir(V). The only O-donor ligand efficient to stabilize Ir(I), Ir(III), and Ir(V), previously reported, is the tridentate tris(diphenyloxophosphoranyl)methanide.[5c]

7. Addition of $HSiEt_3$ to PhC≡CH Catalyzed by Ir(acac)H($SiEt_3$)(PCy_3). The addition of silanes to

(31) (a) Oro, L. A.; Carmona, D.; Esteruelas, M. A.; Foces-Foces, C.; Cano, F. H. *J. Organomet. Chem.* **1983**, *258*, 357. (b) Oro, L. A.; Carmona, D.; Esteruelas, M. A.; Foces-Foces, C.; Cano, F. H. *J. Organomet. Chem.* **1986**, *307*, 83.

(32) (a) Deutsch, P. P.; Eisemberg, R. J. *Am. Chem. Soc.* **1990**, *112*, 714. (b) Deutsch, P. P.; Eisenberg, R. *Organometallics* **1990**, *9*, 709. (c) Cleary, B. P.; Mehta, R.; Eisenberg, R. *Organometallics* **1995**, *14*, 2297.

(33) Hlatky, G. G.; Crabtree, R. H. *Coord. Chem. Rev.* **1985**, *65*, 1.

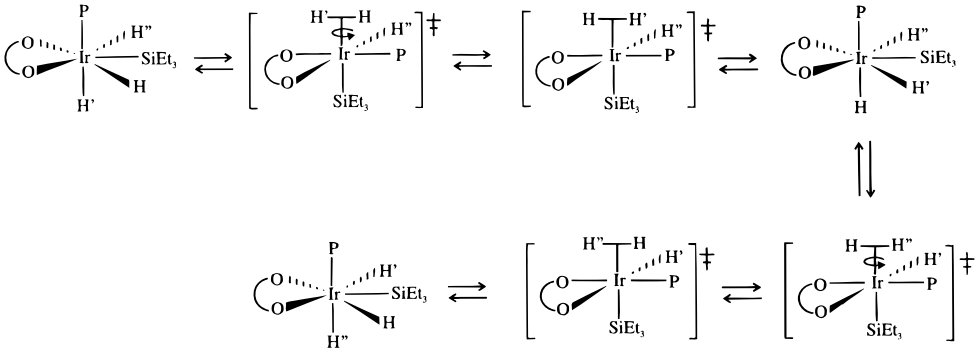
(34) Gilbert, T. M.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 3508.

(35) Loza, M.; Faller, J. W.; Crabtree, R. H. *Inorg. Chem.* **1995**, *34*, 2937.

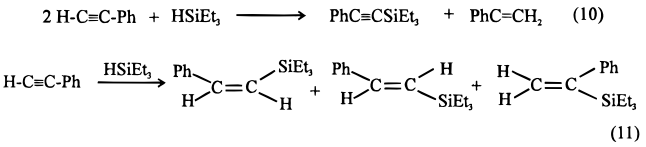
Table 4. Hydrosilylation of Phenylacetylene Catalyzed by Ir(acac)H(PCy$_3$)(SiEt$_3$)

			product ratios			
T, °C	[PhC≡CH], M	[HSiEt$_3$], M	PhC≡CSiEt$_3$	PhSiEt$_3$C=CH$_2$	*cis*-PhCH=CH(SiEt$_3$)	*trans*-PhCH=CH(SiEt$_3$)
23	0.24	0.24	0.101	0.070	0.629	0.200
34	0.24	0.24	0.080	0.040	0.690	0.190
60	0.24	0.24	0.054	0.015	0.718	0.213
60	0.24	0.12	0.136	0.058	0.652	0.154
60	0.24	0.18	0.086	0.035	0.692	0.187
60	0.12	0.24	0.014	0.004	0.671	0.311
60	0.18	0.24	0.022	0.010	0.677	0.291
60	0.36	0.24	0.071	0.016	0.766	0.147

Scheme 3



alkynes catalyzed by transition metal complexes is one of the most important laboratory and industrial methods of forming vinylsilanes,[36] which have shown to be versatile intermediates in organic synthesis.[37] Complex **8** catalyzes the hydrosilylation of phenylacetylene with triethylsilane. The reactions were performed in 1,2-dichloroethane solutions, and the results are listed in Table 4. In all experiments carried out, PhCH=CH$_2$, PhC≡CSiEt$_3$, *cis*-PhCH=CH(SiEt$_3$), *trans*-PhCH=CH(SiEt$_3$), and Ph(SiEt$_3$)C=CH$_2$ were obtained. The quantity of PhCH=CH$_2$ formed is very similar to that of PhC≡CSiEt$_3$. This can be rationalized in terms of a dehydrogenative silylation (eq 10), along with a normal hydrosilylation (eq 11). The rate and extent of the reactions are unaffected by the presence of hydroquinone, suggesting that the participation of radical-like species as catalytic intermediates is not significant.



The major product in all cases is the thermodynamically less stable *cis*-PhCH=CH(SiEt$_3$), resulting from the *anti*-addition of the silane to the alkyne. Contact with the catalyst in the presence of silane leads to isomerization to the more stable *trans*-isomer. Table 4 shows that lowering the triethylsilane concentration or increasing the phenylacetylene concentration increases the relative amount of *cis*-PhCH=CH(SiEt$_3$). The same behavior has been previously observed for the osmium catalyst OsHCl(CO)(P^{i}Pr$_3$)$_2$.[38] Raising temperature also increases the yield of the *cis* isomer. This agrees with the behavior of OsHCl(CO)(P^{i}Pr$_3$)$_2$ but is in contrast with that observed in the presence of the complexes IrH$_2$(SiEt$_3$)(TFB)(PR$_3$) (PR$_3$ = PPh$_3$, P^{i}Pr$_3$, PCy$_3$)[39] and [IrH(H$_2$O)(bq)(PPh$_3$)$_2$]SbF$_6$ (bq = 7,8-benzoquinolato),[40] where raising the temperature favors the *syn*-addition, resulting in the *trans*-isomer.

The mechanisms previously proposed[5b,38,41] for the formation of the *anti*-addition product involve the initial insertion of the alkyne into a M−Si bond to give a (*Z*)-silylvinyl intermediate, which isomerizes to the less sterically congested *E*-isomer via a zwitterionic carbene complex. In addition *β*-elimination of the *endo*-hydrogen atom of the (*E*)-silylvinyl group could lead to the dehydrogenative silylation product PhC≡CSiEt$_3$. The results collected in Table 4 can be rationalized according to this proposal, although the participation of alkynyl intermediates cannot be completely rejected. In this context, it should be mentioned that a recent study on the addition of triethylsilane to phenylacetylene catalyzed by [Ir(COD)(η^2-^{i}Pr$_2$CH$_2$CH$_2$OMe)]BF$_4$ has revealed that under the catalytic conditions both hydrido−alkynyl and hydrido−silyl intermediates are formed.[42]

Concluding Remarks

The complex Ir(acac)(cyclooctene)(PCy$_3$) reacts with HER$_3$ to give the five-coordinate derivatives Ir(acac)H(ER$_3$)(PCy$_3$) (E = Si, Sn). The determination of the structure of Ir(acac)H(SiEt$_3$)(PCy$_3$) by X-ray diffraction

(36) Noels, A. F.; Hubert, A. J. *Industrial Aplications of Homogeneous Catalysis*, Mortreux, A., Petit, F., Eds.; D. Reidel Publishing Co.: Boston, MA, 1988; Chapter 3.1.3.

(37) (a) Hudrlik, P. F. *New Applications of Organometallic Reagents in Organic Synthesis*; Seyferth, D., Ed.; Elsevier: Amsterdam, 1976; p 127. (b) Chan. T. H. *Acc. Chem. Res.* **1977**, *10*, 442. (c) Cook, F.; Moerch, J.; Schwindeman, J.; Magnus, P. *J. Org. Chem.* **1980**, *45*, 1406. (d) Fleming, I.; Dunogues, J.; Swithers, R. H. *Org. React.* **1989**, *37*, 57.

(38) Esteruelas, M. A.; Oro, L. A.; Valero, C. *Organometallics* **1991**, *10*, 462.

(39) Esteruelas, M. A.; Nürnberg, O.; Oliván, M.; Oro, L. A.; Werner, H. *Organometallics* **1993**, *12*, 3264.

(40) Jun, C. H.; Crabtree, R. H. *J. Organomet. Chem.* **1993**, *447*, 177.

(41) (a) Ojima, I.; Clos, N.; Donovan, R. J.; Ingallina, P. *Organometallics* **1990**, *9*, 3127. (b) Esteruelas, M. A.; Herrero, J.; Oro, L. A. *Organometallics* **1993**, *12*, 2377.

(42) Esteruelas, M. A.; Oliván, M.: Oro, L. A.; Tolosa, J. I. *J. Organomet. Chem.* **1995**, *487*, 143.

has revealed that these compounds have a square pyramidal arrangement of ligands around the metallic center, in contrast to that observed for related five-coordinate compounds containing only monodentate ligand, where the arrangement of ligands around the iridium atom is trigonal bipyramidal.

In the presence of triyclohexylphosphine the complex Ir(acac)(cyclooctene)(PCy_3) reacts not only with silanes and stannanes but also with terminal alkynes and molecular hydrogen, to afford the six-coordinate complexes Ir(acac)HX(PCy_3)$_2$ (X = Si, Sn, C_2R, H). These reactions most probably involve reaction intermediates where the acetylacetonato ligand is coordinated in a η^1-C^3(acac) fashion.

An especially interesting reaction takes places when the complex Ir(acac)(cyclooctene)(PCy_3) is treated with 3 equiv of phenylacetylene. Under these conditions the unusual Ir{κ^3-CH=C(Ph)CH[C(O)CH_3]$_2$}(C_2Ph)(CPh=CH_2)(PCy_3) complex is obtained. The formation of this compound involves the oxidative addition of the HC≡ bond of an alkyne, the insertion of a second alkyne into a Ir-η^1-C^3(acac) bond, and the insertion of a third alkyne into a Ir−H bond, on the same metallic center. The three reactions together on the same metallic atom have no precedent. Furthermore, it should be noted that, although, the 1,4-addition of activate alkynes across the β-ketoenolato−iridium and −rhodium rings have been previously described, nothing was known about this reaction with nonactivating terminal alkynes.

Under atmospheric presence of hydrogen, the complex Ir(acac)H($SiEt_3$)(PCy_3) affords the trihydrido−silyl derivative Ir(acac)H_3($SiEt_3$)(PCy_3), which is the only example of compound of this type with an O-donor ligand. Under argon atmosphere the complex Ir(acac)H($SiEt_3$)(PCy_3) also catalyzes the addition of triethylsilane to phenylacetylene to give *cis*-PhCH=CH($SiEt_3$) with selectivities of about 70%.

In conclusion, this study has revealed that the acetylacetonato ligand stabilizes not only iridium(I) and iridium(III) but also iridium(V) derivatives. Furthermore, it promotes catalytic activity in the selective *anti*-addition of triethylsilane to phenylacetylene. The only O-donor ligand previously reported with a similar behavior is the tridentate tris(diphenyloxophosphoranyl)methanide.

Experimental Section

General Considerations. All reactions were carried out under an argon atmosphere using Schlenk tube techniques. Solvents were dried and purified by known procedures and distilled under argon prior to use. The starting complex Ir(acac)(cyclooctene)(PCy_3) (**1**) was prepared by a published method.[10] Elemental analyses were performed with a Perkin-Elmer 240 XL microanalyzer. NMR spectra were recorded on a Varian 200 XL or on a Varian UNITY 300. Chemical shifts are expressed in parts per million, upfield from $Si(CH_3)_4$ ($^{13}C\{^1H\}$, ^1H) and 85% H_3PO_4 ($^{31}P\{^1H\}$). Infrared spectra were run on a Perkin-Elmer 783 instrument.

Preparation of Ir(acac)H_2(PCy_3)$_2$ (2). A solution of **1** (110 mg, 0.16 mmol) in toluene (10 mL) was treated with PCy_3 (45 mg, 0.16 mmol), and a slow stream of H_2 was passed through the solution for 30 min at room temperature. The resulting solution was filtered through Kieselguhr, and the filtrate was concentrated to ca. 0.1 mL; addition of hexane precipitated a white solid. The solvent was decanted, and the solid was twice washed with hexane and dried in vacuo, yield 89 mg (65%). Anal. Calcd for $C_{41}H_{75}IrO_2P_2$: C, 57.65; H, 8.84. Found: C, 57.40; H, 8.99. IR (Nujol cm^{-1}): ν(Ir−H) 2240, 2175; ν(acac) 1590, 1520. $^{31}P\{^1H\}$ NMR (80 MHz, C_6D_6) δ 15.8 (s).

Preparation of Ir(acac)(η^2-HC≡CPh)(PCy_3) (3). A solution of **1** (30 mg, 0.04 mmol) in benzene-d_6 (0.6 mL) contained in a 5-mm NMR tube was treated with HC≡CPh (5 μL, 0.04 mmol). After 5 min the ^1H and $^{31}P\{^1H\}$ NMR show signals corresponding to **3** and free cyclooctene. ^1H NMR (300 MHz, C_6D_6, 295 K) (δ): 8.20−7.00 (m, 5 H, Ph); 5.60 (m, 2 H, free coe), 5.22 (s, 1 H, C*H* of acac), 4.10 (s, 1 H, *H*C≡CPh); 2.25−1.22 (m, 45 H, Cy and free coe); 1.85 and 1.50 (both s, 6 H, CH_3 of acac). $^{31}P\{^1H\}$ NMR (121.45 MHz, C_6D_6): δ 7.5 (s).

Preparation of Ir{κ^3-CH=C(Ph)CH[C(O)CH_3]$_2$}(C_2Ph)(CPh=CH_2)(PCy_3) (4). PhC≡CH (46 μL, 0.42 mmol) was added to a orange solution of **1** (98 mg, 0.14 mmol) in toluene (10 mL). The resulting red solution was stirred for 1 h at room temperature and the solvent removed in vacuo. Addition of hexane caused the precipitated an orange solid. The solvent was decanted, and the solid was twice washed with hexane and then dried in vacuo, yield 90 mg (73%). Anal. Calcd for $C_{47}H_{58}IrO_2P$: C, 64.42; H, 6.44. Found: C, 64.26: H, 6.29. IR (Nujol, cm^{-1}): ν(C≡C) 2106; ν(CO) 1658, 1593; ν(C=C) 1548. ^1H NMR (300 MHz, $CDCl_3$) (δ): 9.15 (s, 1 H, *H*C=CPh); 7.44−6.81 (m, 15 H, Ph); 5.79 (s, 1 H, C*H* of acac); 5.69 and 5.19 (both t, 2 H, J_{P-H} = 5 Hz, J_{H-H} = 3 Hz, PhC=CH_2); 2.58 and 2.26 (both s, 6 H, CH_3); 2.54−1.00 (m, 33 H, Cy). $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$, 295 K) (δ): 209.38 and 207.37 (both s, *C*O); 166.93 (d, J_{P-C} = 92 Hz, H*C*=CPh); 153.92 (s, PhC=*C*H_2); 141.71 (d, J_{P-C} = 6 Hz, HC=*C*Ph); 131.55 (s, Ph); 131.13 (s, C≡*C*Ph); 128.78 (s, Ph); 128.02 (s, Ph); 127.63 (s, Ph); 126.51 (s, Ph); 126.46 (s, Ph); 125.81 (d, J_{P-C} = 4 Hz, *C*≡CPh); 125.63 (s, Ph); 124.17 (s, Ph); 123.79 (s, Ph); 119.99 (d, J_{P-C} = 4 Hz, Ph*C*=CH_2); 75.06 (s, *C*H of acac); 33.99 (d, J_{P-C} = 18 Hz, P*C*HCH_2); 33.02 and 32.42 (both s, *C*H_3); 29.59 and 29.45 (both s, *C*H_2); 28.30 and 28.18 (both d, J_{P-C} = 10 Hz, PCH*C*H_2); 27.22 (s, *C*H_2). $^{31}P\{^1H\}$ NMR (80 MHz, $CDCl_3$): δ −2.53 (s).

Preparation of Ir(acac)H(C≡CPh)(PCy_3)$_2$ (5). A solution of **1** (98 mg, 0.14 mmol) in toluene (10 mL) was treated with PCy_3 (40 mg, 0.14 mmol) and PhC≡CH (16 μL, 0.14 mmol). The resulting solution was stirred for 6 h at room temperature and filtered through Kieselguhr. The filtrate was concentrated to ca. 0.1 mL; addition of methanol caused the precipitation of a white solid. The solvent was decanted, and the solid was twice washed with methanol and dried in vacuo, yield 69 mg (52%). Anal. Calcd for $C_{49}H_{79}IrO_2P_2$: C, 61.67; H, 8.33. Found: C, 61.96; H, 8.20. IR (Nujol, cm^{-1}): ν(Ir−H) 2260; ν(C≡C) 2120; ν(acac) 1580, 1520. $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$, 295 K) (δ): 187.52 and 182.39 (both s, *C*O of acac); 130.96 (s, C≡*C*Ph); 129.56 (s, $C_{o\text{-Ph}}$); 127.26 (s, $C_{m\text{-Ph}}$); 127.26 (t, J_{P-C} = 11 Hz, *C*≡CPh); 125.77 (s, $C_{p\text{-Ph}}$); 101.08 (s, *C*H of acac); 31.15 (d, J_{P-C} = 15 Hz, P*C*HCH_2); 28.15 and 228.96 (both s, *C*H_2); 27.52 (d, J_{P-C} = 10 Hz, PCH*C*H_2); 23.75 (s, *C*H_3 of acac); 26.08 (s, *C*H_2). $^{31}P\{^1H\}$ NMR (80 MHz, $CDCl_3$): δ 29.8 (s).

Preparation of Ir(acac)H(C≡CCy)(PCy_3)$_2$ (6). The complex was prepared using the procedure described for **5**, starting from **1** (110 mg, 0.16 mmol), PCy_3 (45 mg, 0.16 mmol), and CyC≡CH (20 μL, 0.16 mmol). Complex **6** was isolated as a pale yellow solid, yield 76 mg (50%). Anal. Calcd for $C_{49}H_{85}IrO_2P_2$: C, 61.29; H, 8.91. Found: C, 61.57; H, 8.96. IR (Nujol, cm^{-1}): ν(Ir−H) 2263; ν(C≡C) 2165; ν(acac) 1595, 1515. $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$) (δ): 185.33 and 181.64 (both s, *C*O of acac); 129.99 (s, C≡*C*Cy); 128.00 (t, J_{P-C} = 13 Hz, *C*≡CCy); 101.32 (s, *C*H of acac); 32.90 and 32.58 (both d, J_{P-C} = 13 Hz, P*C*HCH_2); 28.06 (s, Cy); 28.87 and 28.64 (both s, *C*H_2); 28.01 (s br, PCH*C*H_2); 26.86 (s, Cy); 26.00 (s, Cy); 25.83 (s, *C*H_3 of acac); 25.67 (s, Cy); 25.32 (s, *C*H_2). $^{31}P\{^1H\}$ NMR (121.45 MHz, $CDCl_3$): δ 14.7 (s).

Preparation of Ir(acac)H(C≡CSiMe_3)(PCy_3)$_2$ (7). The complex was prepared using the procedure described for **5**, starting from **1** (100 mg, 0.15 mmol), PCy_3 (41 mg, 0.15 mmol), and Me_3SiC≡CH (21 μL, 0.15 mmol). Complex **7** was isolated

Table 5. Atomic Coordinates ($\times 10^4$; $\times 10^5$ for Ir and P Atoms) and Equivalent Isotropic Displacement Coefficients (Å^2 $\times$ 10^3; Å^2 $\times$ 10^4 for Ir and P Atoms) for the Compound Ir{κ^3-CH=C(Ph)CH[C(O)(CH$_3$]$_2$}-(C$_2$Ph)(CPh=CH$_2$)(PCy$_3$) (4)

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}[a]/U_{iso}[b]
Ir	61074(2)	29465(3)	0	199(1)
P	63357(14)	39631(21)	8383(9)	193(5)
O(1)	6872(4)	1561(7)	207(3)	24(2)
O(2)	7216(5)	3613(6)	−321(3)	28(2)
C(1)	7341(6)	1214(11)	−140(3)	27(3)
C(2)	7755(6)	204(9)	−41(9)	40(3)
C(3)	7420(7)	1822(10)	−682(4)	31(3)
C(4)	7654(5)	3008(11)	−570(4)	28(2)
C(5)	8421(7)	3392(12)	−777(5)	40(3)
C(6)	6038(6)	2235(8)	−751(4)	24(2)
C(7)	6645(6)	1809(8)	−1000(4)	25(2)
C(8)	6651(6)	1318(9)	−1562(4)	25(2)
C(9)	6135(8)	1765(9)	−1965(4)	36(2)
C(10)	6089(9)	1277(11)	−2482(4)	44(3)
C(11)	6530(8)	359(11)	−2604(5)	42(3)
C(12)	7029(8)	−72(12)	−2230(5)	45(3)
C(13)	7100(8)	411(11)	−1698(5)	42(3)
C(14)	5462(6)	4048(9)	−305(4)	25(2)
C(15)	5046(7)	4766(11)	−538(4)	32(3)
C(16)	4596(7)	5579(10)	−796(5)	30(2)
C(17)	4433(9)	6550(13)	−541(5)	51(4)
C(18)	3994(10)	7379(14)	−797(9)	76(6)
C(19)	3693(8)	7223(21)	−1299(9)	88(8)
C(20)	3836(11)	6245(21)	−1568(8)	88(7)
C(21)	4285(11)	5409(17)	−1321(7)	47(5)
C(22)	5154(6)	2175(9)	281(4)	24(2)
C(23)	4442(6)	2637(10)	373(4)	34(3)
C(24)	5198(6)	943(10)	419(5)	31(2)
C(25)	5411(7)	204(9)	−5(11)	50(3)
C(26)	5456(12)	−917(12)	135(9)	84(8)
C(27)	5264(11)	−1294(14)	659(10)	84(6)
C(28)	5056(11)	−549(14)	1066(8)	74(6)
C(29)	5023(9)	597(12)	926(6)	52(4)
C(30)	6980(6)	5165(9)	692(4)	27(2)
C(31)	7228(7)	5854(9)	1177(4)	32(2)
C(32)	7885(7)	6630(11)	1028(5)	40(3)
C(33)	7662(8)	7339(10)	527(5)	44(3)
C(34)	7397(7)	6662(10)	56(7)	41(3)
C(35)	6717(7)	5910(9)	218(4)	29(2)
C(36)	5469(5)	4420(8)	1233(4)	18(2)
C(37)	5568(6)	4681(10)	1838(4)	28(2)
C(38)	4788(6)	4947(10)	2115(4)	31(2)
C(39)	4376(7)	5879(11)	1825(5)	42(3)
C(40)	4270(10)	5626(15)	1210(7)	42(4)
C(41)	5059(7)	5398(9)	947(4)	28(2)
C(42)	6908(5)	3218(8)	1370(4)	20(2)
C(43)	6460(6)	2167(10)	1536(4)	30(2)
C(44)	6892(8)	1562(11)	2000(5)	40(3)
C(45)	7704(8)	1292(12)	1829(5)	44(3)
C(46)	8143(6)	2326(10)	1653(5)	34(3)
C(47)	7744(6)	2950(10)	1203(4)	27(2)
C1(1)	5088(3)	8229(5)	−2420(2)	80(2)
C(80)	5150(8)	8917(16)	−1782(6)	59(4)
Cl(2)	4422(4)	9888(5)	−1727(3)	121(3)
Cl(3)	8908(4)	2144(5)	−2180(2)	100(2)
C(81)	8119(8)	2578(15)	−2549(6)	95(7)
Cl(4A)[b]	8192(12)	3512(10)	−3043(5)	86(5)
Cl(4B)[b]	8541(13)	3372(11)	−3114(5)	95(5)
Cl(5A)[b]	7258(9)	4887(11)	−1731(5)	111(4)
C(82A)[b]	6435(11)	5570(14)	−1478(13)	76(9)
Cl(6A)[b]	6628(10)	6983(12)	−1497(7)	120(5)
Cl(5B)[b]	6873(9)	4553(11)	−1813(5)	75(4)
C(82B)[b]	6805(32)	5433(24)	−1251(9)	87(15)
Cl(6B)[b]	6434(21)	6701(19)	−1456(15)	185(16)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] Atoms involved in solvent disorder.

as a white solid, yield 69 mg (48%). Anal. Calcd for $C_{46}H_{83}IrO_2P_2Si$: C, 58.11; H, 8.84. Found: C, 58.90: H; 9.20. IR (Nujol cm^{-1}): ν(Ir−H) 2275; ν(C≡C) 2040; ν(acac) 1595, 1513. $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$, 295 K) (δ): 184.25 and 181.92 (both s, *C*O of acac); 129.81 (t, J_{P-C} = 8 Hz, *C*≡CSiMe$_3$); 127.08 (s, C≡*C*SiMe$_3$); 99.95 (s, *C*H of acac); 29.95 (d, J_{P-C} = 28 Hz, P*C*HCH$_2$); 29.15 and 28.96 (both s, *C*H$_2$); 26.56 (d, J_{P-C} = 10 Hz, PCH*C*H$_2$); 25.9 (s, *C*H$_3$ of acac); 24.99 (s, *C*H$_2$); 0.53 (s, Si*C*H$_3$). $^{31}P\{^1H\}$ NMR (121.45 MHz, $CDCl_3$): δ 14.9 (s).

Table 6. Atomic Coordinates ($\times 10^4$; $\times 10^5$ for Ir, P, and Si) and Equivalent Isotropic Displacement Coefficients (Å^2 $\times$ 10^3; Å^2 $\times$ 10^4 for Ir, P, and Si Atoms) for the Compound Ir(acac)H(SiEt$_3$)-(PCy$_3$)(8)

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}[a]
Ir	12161(1)	110075(1)	0	115(1)
P	10496(4)	125203(8)	12691(11)	117(2)
Si	8244(4)	96323(9)	12917(11)	149(2)
O(1)	2021(1)	11321(2)	87(4)	16(1)
O(2)	1369(1)	9856(2)	−1538(3)	17(1)
C(1)	2369(2)	10820(3)	−634(4)	17(1)
C(2)	2915(2)	11189(4)	−347(4)	22(1)
C(3)	2283(2)	9999(3)	−1605(4)	18(1)
C(4)	1806(2)	9579(3)	−2013(4)	17(1)
C(5)	1780(2)	8690(4)	−3124(5)	27(1)
C(6)	670(1)	8385(3)	150(6)	19(1)
C(7)	405(2)	7414(3)	925(4)	24(1)
C(8)	1296(2)	9072(4)	2600(5)	25(1)
C(9)	1824(2)	8766(5)	2002(6)	36(1)
C(10)	204(2)	9948(4)	2222(4)	19(1)
C(11)	−264(2)	10149(4)	1289(5)	23(1)
C(12)	1290(1)	12654(3)	3061(4)	15(1)
C(13)	1861(1)	12317(3)	3166(4)	16(1)
C(14)	2064(2)	12533(3)	4619(4)	17(1)
C(15)	1749(2)	11908(4)	5700(4)	21(1)
C(16)	1185(2)	12241(4)	5593(5)	23(1)
C(17)	978(2)	12014(3)	4141(4)	18(1)
C(18)	366(1)	12965(3)	1377(4)	14(1)
C(19)	126(1)	13165(3)	−36(6)	19(1)
C(20)	−458(1)	13345(3)	51(7)	22(1)
C(21)	−588(2)	14296(4)	1004(4)	24(1)
C(22)	−350(2)	14099(4)	2422(5)	24(1)
C(23)	235(2)	13951(3)	2313(4)	20(1)
C(24)	1425(2)	13648(3)	390(4)	12(1)
C(25)	1390(2)	13591(4)	−1174(4)	18(1)
C(26)	1803(2)	14323(4)	−1828(4)	22(1)
C(27)	1777(2)	15518(4)	−1340(4)	24(1)
C(28)	1790(2)	15580(4)	250(5)	26(1)
C(29)	1378(2)	14844(3)	899(4)	21(1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Preparation of Ir(acac)H(SiEt$_3$)(PCy$_3$) (8). HSiEt$_3$ (24 μL, 0.15 mmol) was added to a solution of **1** (102 mg, 0.15 mmol) in toluene (15 mL). The resulting light yellow solution was stirred for 30 min at room temperature and filtered through Kieselguhr. The filtrate was concentrated to ca. 0.1 mL and the oily residue which formed dissolved in 5 mL of acetone and cooled at −20 °C for 12 h. Complex **8** was isolated as a yellow microcristalline solid, yield 96 mg (93%). Anal. Calcd for $C_{29}H_{56}IrO_2PSi$: C, 50.63; H, 8.20. Found: C, 50.61; H, 8.34. IR (Nujol, cm^{-1}): ν(Ir−H) 2210; ν(acac) 1575, 1520. $^{31}P\{^1H\}$ NMR (121.45 MHz, C_6D_6): δ 9.2 (s).

Preparation of Ir(acac)H(SiPh$_3$)(PCy$_3$) (9). The complex was prepared using the procedure described for **8**, starting from **1** (100 mg, 0.15 mmol) and HSiPh$_3$ (39 mg, 0.15 mmol). Complex **9** was isolated as a light yellow solid, yield 68 mg (55%). Anal. Calcd for $C_{41}H_{56}IrO_2P_2Si$: C, 59.17; H, 6.78. Found: C, 58.96; H, 6.85. IR (Nujol, cm^{-1}): ν(Ir−H) 2202; ν(acac) 1565, 1523. ^1H NMR (300 MHz, C_6D_6, 295 K) (δ): 8.06−7.16 (m, 15 H, Ph); 5.21 (s, 1 H, C*H* of acac); 2.20−0.95 (m, 33 H, Cy); 1.78 (s, 6 H, C*H*$_3$ of acac); −22.81 (d, 1 H, J_{P-H} = 17 Hz, Ir−H). $^{31}P\{^1H\}$ NMR (121.45 MHz, C_6D_6): δ 6.0 (s).

Preparation of Ir(acac)H(SiHPh$_2$)(PCy$_3$) (10). A solution of **1** (20 mg, 0.03 mmol) in benzene-d_6 (0.6 mL) contained in a 5-mm NMR tube was treated with H_2SiPh_2 (6 μL, 0.03 mmol). After 5 min the ^1H and $^{31}P\{^1H\}$ NMR show signals corresponding to **10** and free cyclooctene. $^{31}P\{^1H\}$ NMR (121.45 MHz, C_6D_6): δ 11.9 (s).

Table 7. Crystal Data and Data Collection and Refinement for Ir{κ^3-CH=C(Ph)CH[C(O)CH_3]$_2$}(C_2Ph)(CPh=CH_2)(PCy_3) (4) and Ir(acac)H($SiEt_3$)(PCy_3) (8).

	4	8
	Crystal Data	
formula	$C_{47}H_{58}IrO_2P\cdot 3CH_2Cl_2$	$C_{29}H_{56}IrO_2PSi$
mol wt	1132.97	688.04
color and habit	orange, prismatic bloc	yellow, prismatic bloc
cryst size, mm	0.28 × 0.38 × 0.64	0.36 × 0.36 × 0.38
cryst syst	orthorhombic	orthorhombic
space group	$Pna2_1$ (No. 33)	$Pna2_1$ (No. 33)
a, Å	17.260(2)	25.909(5)
b, Å	12.207(2)	11.984(2)
c, Å	24.376(2)	9.721(2)
Z	4	4
D(calcd), g cm^{-1}	1.465	1.514
	Data Collection and Refinement	
diffractometer	four-circle Siemens-P4	four-circle Siemens-STOE AED-2
λ(M_o Kα), Å; technique	0.710 73; bisecting geometry	
monochromator	graphite oriented	
μ, mm^{-1}	2.97	4.52
scan type	ω	$\omega/2\theta$
2θ range, deg	$2 \le 2\theta \le 50$	$3 \le 2\theta \le 50$
temp, K	173	120
no. of data collcd	11 192	9424
no. of unique data	9025 (R_{int} = 0.0580)	5333 (R_{int} = 0.0267)
no. of params refined	542	312
R_1[a] [$F^2 > 2\sigma(F^2)$]	0.0453	0.0198
wR_2[b] [all data]	0.1148	0.050
S[c]	1.450	0.995
Flack param	−0.03(1)	−0.028(6)

[a] $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2(F^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. [c] Goof = $S = [\sum[w((F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$.

Preparation of Ir(acac)H($SiEt_3$)(PCy_3)$_2$ (11). The complex was prepared using the procedure described for **5**, starting from **1** (102 mg, 0.15 mmol), PCy_3 (47 mg, 0.17 mmol), and $HSiEt_3$ (27 μL, 0.17 mmol). Complex **11** was isolated as a white solid, yield 96 mg (66%). Anal. Calcd for $C_{47}H_{89}IrO_2P_2Si$: C, 58.29; H, 9.26. Found: C, 58.05; H, 9.21. IR (Nujol, cm^{-1}): ν(Ir−H) 2228; ν(acac) 1590, 1510. $^{31}P\{^1H\}$ NMR (121.45 MHz, C_6D_6): δ 13.9 (s).

Preparation of Ir(acac)H($SiHPh_2$)(PCy_3)$_2$ (12). The complex was prepared using the procedure described for **5**, starting from **1** (100 mg, 0.15 mmol), PCy_3 (42 mg, 0.15 mmol), and H_2SiPh_2 (27 μL, 0.15 mmol). Complex **12** was isolated as a white solid, yield 86 mg (55%). Anal. Calcd for $C_{53}H_{85}IrO_2P_2Si$: C, 61.42; H, 8.26. Found: C, 61.28; H, 8.34. IR (Nujol, cm^{-1}): ν(Ir−H) 2210; ν(Si−H) 2065; ν(acac) 1587, 1512. $^{31}P\{^1H\}$ NMR (121.45 MHz, C_6D_6): δ 9.4 (s).

Preparation of Ir(acac)(SiH_2Ph)H(PCy_3)$_2$ (13). The complex was prepared using the procedure described for **5**, starting from **1** (105 mg, 0.15 mmol), PCy_3 (43 mg, 0.15 mmol), and H_3SiPh (18 μL, 0.15 mmol). Complex **13** was isolated as a white solid, yield 60 mg (39%). Anal. Calcd for $C_{47}H_{81}IrO_2P_2Si$: C, 58.79; H, 8.49. Found: C, 58.44; H, 7.95. IR (Nujol, cm^{-1}): ν(Ir−H) 2240; ν(Si−H) 2048, 2090; ν(acac) 1593, 1514. $^{31}P\{^1H\}$ NMR (121.45 MHz, C_6D_6): δ 15.9 (s).

Preparation of Ir(acac)H($SnPh_3$)(PCy_3) (14). A solution of **1** (20 mg, 0.03 mmol) in benzene-d_6 (0.6 mL) contained in a 5-mm NMR tube was treated with $HSnPh_3$ (11 mg, 0.03 mmol). After 5 min the ^1H and $^{31}P\{^1H\}$ NMR show signals corresponding to **14** and free cyclooctene. $^{31}P\{^1H\}$ NMR (121.45 MHz, C_6D_6): δ 7.58 (s, with tin satellites J_{Sn-P} = 44 Hz)

Preparation of Ir(acac)H($SnPh_3$)(PCy_3)$_2$ (15). The complex was prepared using the procedure described for **5**, starting from **1** (100 mg, 0.15 mmol), PCy_3 (41 mg, 0.15 mmol), and $HSnPh_3$ (51.4 mg, 0.15 mmol). Complex **15** was isolated as a pale yellow solid, yield 110 mg (61%). Anal. Calcd for $C_{59}H_{89}IrO_2P_2Sn$: C, 58.92; H, 7.45. Found: C, 58.81; H, 7.34. IR (Nujol, cm^{-1}): ν(Ir−H) 2225; ν(acac) 1590, 1515. $^{31}P\{^1H\}$ NMR (121.45 MHz, C_6D_6): δ 7.62 (s, with tin satellites J^{117}_{Sn-P} = 113 Hz and J^{119}_{Sn-P} = 142 Hz).

Preparation of Ir(acac)H_3($SiEt_3$)(PCy_3) (16). A slow stream of H_2 was passed through a solution of **11** (20 mg, 0.03 mmol) in benzene-d_6 (0.6 mL) contained in a 5-mm NMR tube. After 15 min the ^1H and $^{31}P\{^1H\}$ NMR show signals corresponding to **16**. ^1H NMR (300 MHz, C_6D_6, 295 K) (δ): 5.21 (s, 1 H, C*H* of acac); 2.22−1.11 (m, 48 H, Cy and CH_2CH_3); 1.89 (s, 6 H, CH_3 of acac); −24.00 (br, 3 H, Ir−H). ^1H NMR (300 MHz, C_6D_6, 230 K): AM_2 part of an AM_2X spin system δ_A −3.64 and δ_M 23.26 (J_{A-M} = 0, J_{A-X} = 119.0, J_{M-X} = 19.9). $^{31}P\{^1H\}$ NMR (121.45 MHz, C_6D_6): δ 21.80 (s).

Catalytic Studies. The hydrosilylation reactions were performed under argon at 60 or 20 °C. The reactions were carried out in a two-necked flask fitted with a condenser and a magnetic stirring bar. The second neck was capped with a Suba seal to allow samples to be removed by syringe without opening the system. In a typical procedure, the complex Ir(acac)H($SiEt_3$)(PCy_3)$_2$ were dissolved in a 1,2-dicloroethane solution (4.8 × 10^{-3} M) containing $HSiEt_3$, PhC≡CH, and C_6H_{12}. The flask was then immersed in a bath at 60 °C, and the reaction mixture was magnetically stirred. The reactions were followed by measuring the silane consumption as a function of time using C_6H_{12} as the internal standard with a 15% β,β'-oxobis(propionitrile) on Chromosorb W-HP 80/10-mesh column at 40 °C on a Perkin-Elmer 8500 gas chromatograph with a flame ionization detector. Silicon-containing products were analyzed using a FFAP on Chromosorb GHP 80/10-mesh column a 175 °C. Silicon-containig products were isolated by column chromatography (silica gel 70−230 mesh; hexane) and characterized by ^1H NMR spectroscopy.[42]

X-ray Structure Analysis of Complexes Ir{κ^3-CH=C(Ph)CH[C(O)CH_3]$_2$} (C_2Ph)(CPh=CH_2)(PCy_3) (4) and Ir(acac)H($SiEt_3$)(PCy_3) (8). A summary of crystal data and refinement parameters is reported in Table 7. Atomic coordinates are listed in Tables 5 and 6. Data were collected on Siemens P4 (**4**) or Siemens-Stoe AED-2 (**8**) diffractometers, with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) by the ω (**4**) or $\omega/2\theta$ (**8**) scan methods. Three standard reflections were monitored at periodic intervals throughout data collection; no significant variations were observed. All data were corrected for absorption using an semiempirical[43]

(43) North, A. C. T.; Phillips, D. C.; Matthews, S. F. *Acta Crystallogr., Sect. A* **1968**, *24*, 351.

(**4**) or empirical[44] (**8**) method. All structures were solved by Patterson (iridium atoms) and conventional Fourier techniques and refined by full-matrix least-squares on F^2 (SHELX-93).[45] The function minimized was $\sum[w(F_o^2 - F_c^2)^2]$ with the weight defined as $w^{-1} = [\sigma^2(F_o^2) + (xP)^2 + yP]$ ($P = (F_o^2 + 2F_o^2)/3$). For **4** an empirical extinction correction was applied. Atomic scattering factors, corrected for anomalous dispersion, were used as implemented in the refinement program.

Data for 4. Crystals suitable for the X-ray diffraction study were obtained from slow diffusion of hexane into a saturated CH_2Cl_2 solution of the compound. An orange prismatic bloc of approximate dimensions 0.28 × 0.38 × 0.64 mm was indexed to orthorhombic symmetry. A group of 54 reflections in the range $10 \le 2\theta \le 30°$ were carefully centered and used to obtain by least-squares methods the unit cell dimensions. The hydrogen atoms were calculated (C−H = 0.96 Å) and refined riding on carbon atoms with a common isotropic thermal parameter. Solvent molecules of dichoromethane were observed severely disordered. This molecules exhibit static disorder in three different spatial regions: Cl(1), C(81), and Cl(2); Cl(3), C(82), and Cl(4) (two sites for Cl(4)); Cl(5a)··Cl(6b), with two sites for all atoms. The refinement converged to $R_1 = 0.0453$ [$F^2 > 2\sigma(F^2)$] and w$R_2 = 0.1148$ (all data), with weighting parameters $x = 0.070400$ and $y = 0$ and with an extinction coefficient of 0.000 073. The flack parameter refined to −0.03(1) as an indication of a correct determination of the absolute structure.

(44) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158.
(45) Sheldrick, G. M. J. *Appl. Crystallogr.*, manuscript in preparation.

Data for 8. Crystals suitable for the X-ray diffraction study were obtained from a toluene−acetone solution. A prismatic block of approximate dimensions 0.36 × 0.36 × 0.38 mm was indexed to orthorhombic symmetry. A group of 56 reflections in the range $20 \le 2\theta \le 30°$ were carefully centered and used to obtain by least-squares methods the unit cell dimensions. The hydrogen atoms were localized in a difference map or calculated (C−H = 0.96 Å) and refined riding on carbon atoms with a common isotropic thermal parameter. The hydride atom were refined free from its observed position. The refinement converged to $R_1 = 0.0198$ [$F^2 > 2\sigma(F^2)$] and wR_2 = 0.050 (all data), with weighting parameters $x = 0.03$ and y = 2.0. The flack parameter refined to −0.028(6).

Acknowledgment. We thank the DGICYT (Projet PB 92-0092, *Programa de Promoción General del Conocimiento*, and EU Projet *Selective Processes and Catalysis Involving Small Molecules*) for financial suport. E.O. thanks the DGA (Diputación General de Aragón) for a grant. L.R. thanks the Spanish Government for a grant (Programa de Formación Científica para Iberoamérica).

Supporting Information Available: Tables of anisotropic thermal parameters, atomic coordinates and thermal parameters for hydrogen atoms, experimental details of the X-ray study, bond distances and angles, and selected least-squares planes and interatomic distances (22 pages). Ordering information is given on any current masthead page.

OM950628W