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Novel Hydridoirida-β-diketones Containing Small Molecules, CO, or Ethylene: Their Behavior in Coordinating Solvents Such as Dimethylsulfoxide or Acetonitrile

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New hydridoirida-β-diketones [IrH{(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$H}(CO)]ClO$_4$ **2** and [IrH{(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$H}(olefin)]BF$_4$ (olefin = C$_2$H$_4$, **5**; 1-hexene, **10**) have been prepared. These complexes may afford new diacylhydridoiridium(III) derivatives. In chloroform solution, complex **2** is in equilibrium with the deprotonated diacylhydride *trans*-[IrH(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(CO)] complex **3**. In DMSO, deprotonation of **2** occurs to yield the kinetically favored product **3**, which isomerizes to the thermodynamically favored complex *cis*-[IrH(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(CO)] **4**. Reprotonation of **4** with HBF$_4$ in chlorinated solvents gives the cation in **2**. In coordinating solvents such as dimethyl sulfoxide or acetonitrile, complex **5** undergoes displacement of ethylene to afford [IrH{(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$H}(L)]BF$_4$ (L = DM*S*O, **7**; CH$_3$C*N*, **9**). Complexes **5** and **7** undergo deprotonation by NEt$_3$ to give the corresponding diacylhydrides. The ethylene complex gives only *trans*-[IrH(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(C$_2$H$_4$)] **6**, while the dimethyl sulfoxide derivative affords a mixture of *trans*- and *cis*-[IrH(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(DM*S*O)] **8**. Complex **10** shows inhibited alkene rotation around the Ir–olefin axis. All of the complexes were fully characterized spectroscopically. Single-crystal X-ray diffraction analysis was performed on complexes **3**, **4**, and **9**. The ^{13}C NMR and X-ray data point to a carbenoid character in the carbon atoms bonded to iridium in the irida-β-diketone fragment, so that it can be considered as an acyl(hydroxycarbene) moiety.

Introduction

C−H bond cleavage in aldehydes, promoted by transition metal complexes, is an active area of research.[1] Rhodium and iridium compounds oxidatively add aldehyde C−H bonds to afford acylhydride derivatives,[2] and this type of species are believed to be involved in catalytic processes such as aldehyde decarbonylation or alkene hydroacylation.[3] *o*-(Diphenylphosphino)benzaldehyde (PPh$_2$(*o*-C$_6$H$_4$CHO)) promotes the chelate-assisted oxidative addition of aldehyde to several late transition metals in low oxidation states, yielding cis acylhydride complexes that contain acylphosphine chelates (PPh$_2$(*o*-C$_6$H$_4$CO)).[4] Ir(III) complexes also react with aldehyde C−H bonds to give decarbonylated alkyl or aryl groups, or acylphosphine derivatives when using PPh$_2$(*o*-C$_6$H$_4$CHO) as the source of aldehyde, and these reactions may involve iridium(V) intermediates formed by oxidative addition of aldehyde to Ir(III) species.[5]

The reaction of [Ir(Cl)(H)(PPh$_2$(*o*-C$_6$H$_4$CO))(Cod)] with PPh$_2$(*o*-C$_6$H$_4$CHO) in protic solvents allowed the preparation of the first hydridoirida-β-diketone [IrH{(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$H}Cl] **1a** shown in Chart 1. Most likely, the reaction occurs via an isomeric diacyldihydridoiridium(V) intermedi-

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(1) (a) Marder, T. B.; Roe, D. C.; Milstein, D. *Organometallics* **1988**, *7*, 1451. (b) Gutiérrez-Puebla, E.; Monge, A.; Paneque, M.; Poveda, M. L.; Salazar, V.; Carmona, E. *J. Am. Chem. Soc.* **1999**, *121*, 248. (c) Tellers, D. M.; Bergman, R. G. *Organometallics* **2001**, *20*, 4819.

(2) (a) Thorn, D. L. *Organometallics* **1982**, *1*, 197. (b) Milstein, D. *Organometallics* **1982**, *1*, 1549. (c) Milstein, D.; Fultz, W. C.; Calabrese, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 1336. (d) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Bachechi, F. *Organometallics* **1991**, *10*, 820. (e) Bleeke, J. R.; Haile, T.; New, P. R.; Chiang, M. Y. *Organometallics* **1993**, *12*, 517. (f) Wang, K.; Emge, T. J.; Goldman, A. S.; Li, C.; Nolan, S. P. *Organometallics* **1995**, *14*, 4929. (g) Goikhman, R.; Milstein, D. *Angew. Chem., Int. Ed.* **2001**, *40*, 1119.

(3) (a) Milstein, D. *J. Chem. Soc., Chem. Commun.* **1982**, 1357. (b) Collman, J. P.; Hegedeus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987. (c) Jun, C. H.; Hong, J. B.; Lee, D. Y. *Synlett* **1999**, 1.

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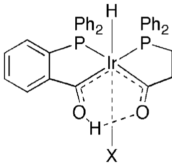
Chart 1



1a; 1b
X = Cl; $OClO_3$

ate $[Ir(Cl)(H)_2(PPh_2(o\text{-}C_6H_4CO))_2]$ formed by oxidative addition of aldehyde to the starting Ir(III) species. The more reactive $[IrH\{(PPh_2(o\text{-}C_6H_4CO))_2H\}(OClO_3)]$ **1b** was also prepared from **1a**.[6] Metalla-β-diketones were synthesized for the first time by Lukehart by the protonation of diacylmetalate anions $[L_xM(COR)(COR')]^-$,[7] and more recently platina-β-diketones have been reported, obtained by the reaction of hexachloroplatinic acid with alkynes or by the reaction of diacylhydridoplatinum(IV) complexes with $TlPF_6$.[8] Metalla-β-diketones can be regarded as acyl(hydroxycarbene) complexes stabilized intramolecularly by hydrogen bonds.[8b,d] Hydroxycarbene complexes, for which a tautomeric equilibrium with the acylhydrides has been reported,[9] are proposed as important intermediates in CO reduction reactions,[10] decarbonylation of aldehydes,[2b] or alkene hydrocarbonylation reactions to produce alcohols.[11]

We report here on the reactions of complexes **1** with carbon monoxide or olefins to afford novel hydridoirida-β-diketones, their characterization, and their behavior in coordinating solvents such as dimethyl sulfoxide or acetonitrile.

Experimental Section

General Procedures. The preparation of the metal complexes was carried out at room temperature under nitrogen by standard Schlenk techniques. $[IrH\{(PPh_2(o\text{-}C_6H_4CO))_2H\}X]$ (X = Cl, **1a** or $OClO_3$, **1b**) was prepared as previously reported.[6] Microanalysis was carried out with a Leco CHNS-932 microanalyzer. Conductivities were measured in acetone solution with a Metrohm 712 conductimeter. IR spectra were recorded with a Nicolet FTIR 740 spectrophotometer in the range 4000−400 cm^{-1} using KBr pellets. NMR spectra were recorded with a Bruker Avance DPX 300 or a Bruker Avance 500 spectrometer; ^1H and $^{13}C\{^1H\}$ (TMS internal standard), $^{31}P\{^1H\}$ (H_3PO_4 external standard), and 2D spectra were measured from $CDCl_3$ or DMSO-d_6 solutions. Mass spectra were recorded on a VG Autospec, by liquid secondary ion (LSI) MS using nitrobenzyl alcohol as matrix and a cesium gun (Universidad de Zaragoza).

Warning: Perchlorate salts and perchlorate transition metal complexes may be explosive. Preparations at a larger scale than that reported herein should be avoided.

Preparation of $[IrH\{(PPh_2(o\text{-}C_6H_4CO))_2H\}(CO)]ClO_4$ (2). Carbon monoxide at room temperature was bubbled for 30 min through a dichloromethane solution of $[IrH\{(PPh_2(o\text{-}C_6H_4CO))_2H\}(OClO_3)]$ (**1b**) (0.06 mmol). The pale yellow complex was precipitated by addition of diethyl ether, filtered off, washed with diethyl ether, and vacuum-dried. IR (cm^{-1}): 2128 (s), υ(Ir−H); 2037 (s), υ(C≡O); 1628 (s), υ(C═O), 1093 (vs), $\upsilon(ClO_4)$. Λ_M (Ω^{-1} cm^2 mol^{-1}): 128. ^1H NMR ($CDCl_3$): δ −9.08 (t, 1H, J(P,H) = 16.6 Hz, IrH), 22.51 (s, br, 1H, OHO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 17.9 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 249.2 (d, J(P,C) = 82 Hz, C═O), 169.0 (t, J(P,C) = 6 Hz, C≡O). FAB MS: calcd for $C_{39}H_{30}IrO_3P_2$, 801; observed, 801 $[M]^+$. Anal. Calcd for $C_{39}H_{30}ClIrO_7P_2\cdot0.5CH_2Cl_2$: C, 50.32; H, 3.31. Found: C, 50.57; H, 3.58.

Preparation of *trans*-$[IrH(PPh_2(o\text{-}C_6H_4CO))_2(CO)]$ (3). To a dichloromethane solution of complex **2** (0.06 mmol) was added a stoichiometric amount of triethylamine (0.06 mmol). After being stirred for 30 min at room temperature, the solution was washed three times with distilled water and dried over magnesium sulfate. Filtration, followed by addition of diethyl ether, gave a yellow solid that was filtered off, washed with diethyl ether, and vacuum-dried. IR (cm^{-1}): 2068 (s), υ(Ir−H); 1990 (s), υ(C≡O); 1645 (s), υ(C═O). ^1H NMR ($CDCl_3$): δ −8.51 (t, 1H, J(P,H) = 18.9 Hz, IrH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 21.1 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 220.7 (d, J(P,C) = 85 Hz, C═O), 174.5 (s, br, C≡O). FAB MS: calcd for $C_{39}H_{29}IrO_3P_2$, 800; observed, 801 $[M + H]^+$. Anal. Calcd for $C_{39}H_{29}IrO_3P_2$: C, 58.57; H, 3.65. Found: C, 58.19; H, 3.21.

Preparation of *cis*-$[IrH(PPh_2(o\text{-}C_6H_4CO))_2(CO)]$ (4). Stirring of a dimethyl sulfoxide solution of complex **2** (0.06 mmol) for 48 h followed by addition of water gave a pale yellow solid that was filtered off, washed with diethyl ether, and vacuum-dried. The solid was recrystallized from $CHCl_3$/diethyl ether. IR (cm^{-1}): 2112 (m), υ(Ir−H); 2023 (s), υ(C≡O); 1623 (s), υ(C═O). ^1H NMR ($CDCl_3$): δ −8.68 (dd, 1H, $J(P,H)_{trans}$ = 110.2 Hz, $J(P,H)_{cis}$ = 17.8 Hz, IrH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 26.1 (d, J(P,P) = 5 Hz), 21.6 (d). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 227.4 (t, J(P,C) = 5 Hz, C═O), 221.4 (d, J(P,C) = 85 Hz, C═O), 175.3 (t, J(P,C) = 5 Hz, C≡O). Anal. Calcd for $C_{39}H_{29}IrO_3P_2\cdot1.75CHCl_3$: C, 48.52; H, 3.07. Found: C, 48.52; H, 3.28.

Preparation of $[IrH\{(PPh_2(o\text{-}C_6H_4CO))_2H\}(C_2H_4)]BF_4$ ([5]-BF_4). Ethylene at room temperature was bubbled for 30 min through a dichloromethane solution of complex $[IrH\{(PPh_2(o\text{-}C_6H_4CO))_2H\}Cl]$ **1a** (0.06 mmol) in the presence of $AgBF_4$ (0.12 mmol). After filtration of the silver salts, the addition of diethyl ether to the solution gave a yellow precipitate that was filtered off, washed with diethyl ether, and vacuum-dried. IR (cm^{-1}): 2149 (m), υ(Ir−H); 1629 (s), υ(C═O); 1080 (vs), $\upsilon(BF_4)$. Λ_M (Ω^{-1} cm^2 mol^{-1}): 127. ^1H NMR ($CDCl_3$): δ −9.19 (t, 1H, J(P,H) = 15.3 Hz, IrH), 2.52

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(4) (a) Rauchfuss, T. B. *J. Am. Chem. Soc.* **1979**, *101*, 1045. (b) Landvatter, E. F.; Rauchfuss, T. B. *Organometallics* **1982**, *1*, 506. (c) Koh, J. J.; Lee, W. H.; Williard, P. G.; Risen, W. M. *J. Organomet. Chem.* **1985**, *284*, 409. (d) Ghilardi, C. A.; Midollini, S.; Moneti, S.; Orlandini, A. *J. Chem. Soc., Dalton Trans.* **1988**, 1833. (e) Bianchini, C.; Meli, A.; Peruzzini, M.; Ramirez, J. A.; Vacca, A.; Vizza, F.; Zanobini, F. *Organometallics* **1989**, *8*, 337. (f) Klein, H. F.; Lemke, U.; Lemke, M.; Brand, A. *Organometallics* **1998**, *17*, 4196. (g) El Mail, R.; Garralda, M. A.; Hernández, R.; Ibarlucea, L.; Pinilla, E.; Torres, M. R. *Organometallics* **2000**, *19*, 5310. (h) El Mail, R.; Garralda, M. A.; Hernández, R.; Ibarlucea, L. *J. Organomet. Chem.* **2002**, *648*, 149. (i) Brockaart, G.; El Mail, R.; Garralda, M. A.; Hernández, R.; Ibarlucea, L.; Santos, J. I. *Inorg. Chim. Acta* **2002**, *338*, 249. (j) Garralda, M. A.; Hernández, R.; Ibarlucea, L.; Pinilla, E.; Torres, M. R.; Zarandona, M. *Inorg. Chim. Acta* **2004**, *357*, 2818.

(5) (a) Luecke, H. F.; Bergman, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 11538. (b) Alaimo, P. J.; Arndtsen, B. A.; Bergman, R. G. *Organometallics* **2000**, *19*, 2130. (c) Nieuwenhuyzen, M.; Saunders, G. C. *Inorg. Chim. Acta* **2004**, *357*, 2870.

(6) Garralda, M. A.; Hernández, R.; Ibarlucea, L.; Pinilla, E.; Torres, M. R. *Organometallics* **2003**, *22*, 3600.

(7) (a) Lukehart, C. M. *Adv. Organomet. Chem.* **1986**, *25*, 45. (b) Lukehart, C. M.; Zeile, J. V. *J. Am. Chem.* Soc. **1976**, *98*, 2365.

(8) (a) Steinborn, D.; Gerish, M.; Merzweiler, K.; Schenzel, K.; Pelz, K.; Bögel, H. *Organometallics* **1996**, *15*, 2454. (b) Gerish, M.; Heinemann, F. W.; Bruhn, C.; Scholz, J.; Steinborn, D. *Organometallics* **1999**, *18*, 564. (c) Nordhoff, K.; Steinborn, D. *Organometallics* **2001**, *20*, 1408. (d) Steinborn, D.; Gerish, M.; Bruhn, C.; Davies, J. A. *Inorg. Chem.* **1999**, *38*, 680.

(9) Casey, C. P.; Czerwinski, C. J.; Fusie, K. A.; Hayashi, R. K. *J. Am. Chem. Soc.* **1997**, *119*, 3971.

(10) Cornils, B., Herrmann, W. A., Eds. *Applied Homogeneous Catalysis with Organometallic Compounds*; VCH: Weinheim, 1996.

(11) Cheliatsidou, P.; White, D. F. S.; Cole-Hamilton, D. J. *J. Chem. Soc., Dalton Trans.* **2004**, 3425.

(s, 4H, C_2H_4), 22.25 (s, 1H, OHO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 20.4 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 256.4 (d, J(P,C) = 85 Hz, C═O), 70.5 (s, C_2H_4). FAB MS: calcd for $C_{40}H_{34}IrO_2P_2$, 801; observed, 801 $[M]^+$. Anal. Calcd for $C_{40}H_{34}BF_4IrO_2P_2 \cdot 0.25CH_2Cl_2$: C, 53.19; H, 3.83. Found: C, 53.38; H, 4.16.

Preparation of $[IrH(PPh_2(o\text{-}C_6H_4CO))_2(C_2H_4)]$ (6). To a dichloromethane solution of compound [**5**]BF_4 (0.06 mmol) was added a stoichiometric amount of triethylamine (0.06 mmol). After being stirred for 30 min at room temperature, the solution was washed three times with distilled water and dried over magnesium sulfate. Filtration, followed by addition of diethyl ether, gave a yellow solid that was filtered off, washed with diethyl ether, and vacuum-dried. IR (cm^{-1}): 2013 (s), υ(Ir−H); 1633 (s), υ(C═O). ^1H NMR ($CDCl_3$): δ −8.90 (t, 1H, J(P,H) = 17.2 Hz, IrH), 2.31 (s, 4H, C_2H_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23.2 (s). Anal. Calcd for $C_{40}H_{33}IrO_2P_2 \cdot 0.5CH_2Cl_2$: C, 57.75; H, 4.07. Found: C, 57.77; H, 4.12.

Preparation of $[IrH\{(PPh_2(o\text{-}C_6H_4CO))_2H\}(DMSO)]BF_4$ (7). To a dichloromethane solution of $[IrH\{(PPh_2(o\text{-}C_6H_4CO))_2H\}Cl]$ **1a** (0.06 mmol) was added a stoichiometric amount of dimethyl sulfoxide (0.06 mmol) in the presence of $AgBF_4$ (0.12 mmol). Stirring for 30 min at room temperature followed by filtration of the silver salts and addition of diethyl ether to the solution gave a yellow precipitate that was filtered off, washed with diethyl ether, and vacuum-dried. IR (cm^{-1}): 2160 (m), υ(Ir−H); 1627 (s), υ(C═O); 1097 (vs, br), υ(S═O) + υ(BF_4). Λ_M (Ω^{-1} cm^2 mol^{-1}): 99. ^1H NMR ($CDCl_3$): δ −15.71 (t, 1H, J(P,H) = 16.3 Hz, IrH), 2.05 (s, 6H, CH_3), 22.61 (s, 1H, OHO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 22.1 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 254.2 (d, J(P,C) = 88 Hz, C═O), 45.2 (s, CH_3). FAB MS: calcd for $C_{40}H_{36}IrO_3P_2S$, 851; observed, 851 $[M]^+$. Anal. Calcd for $C_{40}H_{36}BF_4IrO_3P_2S \cdot 0.5CH_2Cl_2$: C, 49.63; H, 3.81; S, 3.27. Found: C, 49.55; H, 3.59; S, 3.18.

Preparation of $[IrH(PPh_2(o\text{-}C_6H_4CO))_2(DMSO)]$ (8). To a dichloromethane solution of complex **7** (0.06 mmol) was added a stoichiometric amount of triethylamine (0.06 mmol). After being stirred for 30 min at room temperature, the solution was washed twice with distilled water and dried over magnesium sulfate. Filtration, followed by addition of diethyl ether, gave a yellow solid that was filtered off, washed with diethyl ether, and vacuum-dried. IR (cm^{-1}): 2108 (m, br), υ(Ir−H); 1629 (s), υ(C═O); 1114 (s), υ(S═O). Data for **8a**, ^1H NMR ($CDCl_3$): δ −14.78 (t, 1H, J(P,H) = 17.4 Hz, IrH), 2.39 (s, 6H, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 25.0 (s). Data for **8b**, ^1H NMR ($CDCl_3$): δ −8.72 (dd, 1H, $J(P,H)_{trans}$ = 117.0 Hz, $J(P,H)_{cis}$ = 17.4 Hz, IrH), 1.93 (s, 3H, CH_3), 3.46 (s, 3H, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23.7 (d, J(P,P) = 7 Hz), 22.7 (d). Anal. Calcd for $C_{40}H_{35}IrO_3P_2S \cdot 0.5CH_2Cl_2$: C, 54.51; H, 4.06; S, 3.59. Found: C, 54.33; H, 4.20; S, 3.33.

Preparation of $[IrH\{(PPh_2(o\text{-}C_6H_4CO))_2H\}(CH_3CN)]BF_4$ (9). To a dichloromethane solution of $[IrH\{(PPh_2(o\text{-}C_6H_4CO))_2H\}Cl]$ **1a** (0.06 mmol) was added a stoichiometric amount of the acetonitrile (0.06 mmol) in the presence of $AgBF_4$ (0.12 mmol). Stirring for 30 min at room temperature followed by filtration of the silver salts and addition of diethyl ether to the solution gave a yellow precipitate that was filtered off, washed with diethyl ether, and vacuum-dried. IR (cm^{-1}): 2318 (w), υ(C≡N); 2185 (m), υ(Ir−H); 1624 (s), υ(C═O); 1083 (vs), υ(BF_4). Λ_M (Ω^{-1} cm^2 mol^{-1}): 114. ^1H NMR ($CDCl_3$): δ −18.44 (t, 1H, J(P,H) = 14.0 Hz, IrH), 1.56 (s, 3H, CH_3), 22.62 (s, 1H, OHO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 26.0 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 254.7 (d, J(P,C) = 96 Hz, C═O), 119.9 (s, C≡N), 2.3 (s, CH_3). FAB MS: calcd for $C_{40}H_{33}IrNO_2P_2$, 814; observed, 814 $[M]^+$. Anal. Calcd for $C_{40}H_{33}BF_4IrNO_2P_2 \cdot CH_2Cl_2$: C, 49.96; H, 3.58; N, 1.42. Found: C, 49.87; H, 3.56; N, 1.41.

Preparation of $[IrH\{(PPh_2(o\text{-}C_6H_4CO))_2H\}(C_6H_{12})]BF_4$ (10). To a dichloromethane solution of $[IrH\{(PPh_2(o\text{-}C_6H_4CO))_2H\}Cl]$ **1a** (0.06 mmol) was added a 3-fold stoichiometric amount of 1-hexene (0.18 mmol) in the presence of $AgBF_4$ (0.18 mmol). Stirring for 30 min at room temperature followed by filtration of the silver salts and addition of diethyl ether to the solution gave a yellow precipitate that was filtered off, washed with diethyl ether, and vacuum-dried. IR (cm^{-1}): 2160 (w), υ(Ir−H); 1630 (m), υ(C═O); 1083 (vs), υ(BF_4). Λ_M (Ω^{-1} cm^2 mol^{-1}): 104. ^1H NMR ($CDCl_3$): δ −10.41 (dd, 1H, J(P,H) = 14.2 and 16.7 Hz, IrH), 2.35 (m, 2H, ═CH_2), 3.07 (m, 1H, ═CH), 1.9−0.5 (m, 9H, aliphatic protons), 21.94 (s, 1H, OHO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 20.7 (d, J(P,P) = 6 Hz), 20.3(d). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 257.2 (d, J(P,C) = 97 Hz, C═O), 255.2 (d, J(P,C) = 75 Hz, C═O), 94.5 (s, ═CH), 68.8 (s, ═CH_2), 33.7, 33.1, 22.0 (s, −CH_2), 13.6 (s, CH_3). FAB MS: calcd for $C_{44}H_{42}IrO_2P_2$, 857; observed, 773 $[M - C_6H_{12}]^+$. Anal. Calcd for $C_{44}H_{42}BF_4IrO_2P_2 \cdot 0.5CH_2Cl_2$: C, 54.19; H, 4.39. Found: C, 53.88; H, 4.32.

X-ray Structure Determination of 3, 4, and 9. Suitable crystals for X-ray experiments were obtained by slow diffusion of diethyl ether onto chloroform solutions of complexes **3** or **4** or dichloromethane solutions of complex **9**. Data collection was carried out on a Bruker Smart CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) operating at 50 kV and different values of intensity depending on the crystal. In all cases, the data were collected over a hemisphere of the reciprocal space by combination of three exposure sets. Each exposure of 20 or 30 s covered 0.3 in ω. The first 50 frames were recollected at the end of the data collection to monitor crystal decay, and no appreciable decay was observed. A summary of the fundamental crystal and refinement data is given in Table 1.

The structures were solved by Patterson function and conventional Fourier techniques (SHELXS-97).[12] The refinement for the three structures was made by full-matrix least-squares on F^2 (SHELXL-97).[12] For all compounds, anisotropic parameters were used in the last cycles of refinement for all non-hydrogen atoms with some exceptions. Complex **4** crystallizes with two solvent molecules and compound **9** with a molecule of solvent. For **4**, one of the solvent molecules, and for **9**, all fluorine atoms of the BF_4^- anion and the chlorine atoms of the solvent molecule, only three cycles have been refined anisotropically, and in subsequent cycles their thermal parameters were kept constant. The hydrogen atoms were included in calculated positions and refined riding on their respective carbon atoms with the thermal parameter related to the bonded atoms, with some exceptions. The hydride atoms in all cases, the hydrogen atoms of the solvent molecules involved in the hydrogen bond for **3**, and the enolic hydrogen atom for **9** have been found in a difference Fourier and included and refined riding on the Ir atom or included and fixed. These features led to R1 values of 0.0364, 0.0526, and 0.0527 for **3**, **4**, and **9**, respectively. The largest residual peaks in the final difference map are close to the iridium atom in **3** and **9** and in the vicinity of a chlorine atom of a solvent molecule in **4**.

Results and Discussion

The reaction of complex $[IrH\{(PPh_2(o\text{-}C_6H_4CO))_2H\}(OClO_3)]$ **1b** with carbon monoxide leads to the displacement of the perchlorate group to afford the cationic $[IrH\{(PPh_2(o\text{-}C_6H_4CO))_2H\}(CO)]ClO_4$, complex **2**, shown in Scheme 1, as confirmed by IR and conductivity measurements. The

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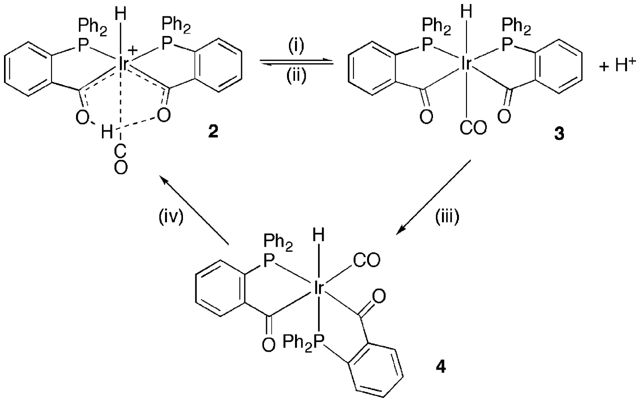
[12] Sheldrick, G. M., *SHELX-97, Program for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1997.

Table 1. Crystal and Refinement Data for **3**, **4**, and **9**

	3	**4**	**9**
formula	$C_{39}H_{29}O_3P_2Ir$	$[C_{39}H_{29}O_3P_2Ir]\cdot 2CHCl_3$	$[C_{40}H_{32}N_1O_2P_2Ir]BF_4\cdot CH_2Cl_2$
M_r	799.76	1038.50	985.55
temp, K	296(2)	296(2)	296(2)
cryst syst	monoclinic	monoclinic	triclinic
space group	*P*2(1)	*P*2(1)/*c*	*P*-1
a, Å	10.9317(8)	21.066(1)	9.8373(7)
b, Å	12.1008(8)	11.1459(7)	13.1332(9)
c, Å	13.168(1)	17.538(1)	16.752(1)
α (deg)			98.297(1)
β (deg)	108.134(1)	90.621(1)	103.212(1)
γ (deg)			102.556(1)
V, $Å^3$	1655.4(2)	4117.6(5)	2013.3(2)
Z	2	4	2
F(000)	788	2040	970
cryst dimens, mm	0.18 × 0.18 × 0.06	0.30 × 0.30 × 0.12	0.16 × 0.15 × 0.12
D(calcd), g cm^{-3}	1.605	1.675	1.624
μ, mm^{-1}	4.166	3.747	3.583
scan technique	φ and ω	φ and ω	φ and ω
data collected	(−11,−15,−17) to (14,16,12)	(−27,−14,−22) to (22,15,23)	(−11,−15,−19) to (11,7,19)
θ	1.63−28.79	1.93−28.80	1.28−25
no. of reflns collected	10 558	25 591	10 576
no. of ind reflns	7399 (R_{int} = 0.029)	9827 (R_{int} = 0.065)	6996 (R_{int} = 0.079)
no. of reflns observed $I > 2\sigma(I)$	6086	6668	4996
R^a (observed reflns)	0.036	0.053	0.053
$R_{wF}{}^b$ (all reflns)	0.073	0.147	0.114

^{a} $\Sigma[|F_0| - |F_c|]/\Sigma|F_0|$. ^{b} $\{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$.

Scheme 1 [a]



[a] (i) DMSO or Et_3N in CH_2Cl_2; (ii) HBF_4 in chlorinated solvents; (iii) protonated DMSO; (iv) HBF_4 in chlorinated solvents.

IR spectrum shows a strong carbonyl absorption at 2037 cm^{-1}, and a sharp absorption at 2128 cm^{-1} due to υ(Ir−H). The trans disposition of both groups is confirmed by the hydride resonance at −9.08 ppm,[13] which appears as triplet due to coupling with two cis phosphorus atoms (*J*(P,H) = 16.6 Hz).

According to the NMR data, the two acylphosphine fragments are equivalent. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 17.9 ppm, and the $^{13}C\{^1H\}$ NMR spectrum shows a doublet in the expected range for Ir(III) species with a certain acyl(hydroxycarbene) character.[6,14] The large *J*(P,C) of 82 Hz confirms the presence of acyl groups trans to phosphorus atoms. Consequently, with these findings, the resonance due to the carbonyl group, at the expected higher field,[15] is a triplet at 169.0 ppm with a small *J*(P,C) of 6 Hz. The O---H---O resonance at low field is extremely broad at room temperature. On lowering the temperature, the signal sharpens and by −40 °C becomes a sharp singlet at 22.51 ppm. The chemical shift of the enolic proton in the cationic species **2** is very close to that of the neutral parent irida-β-diketone **1b**.[6] These chemical shifts appear at slightly lower field than in rhena- or ferra-β-diketones, in the δ 19−21 ppm range,[7] and at even lower field than in platina-β-diketones, in the δ 14−19 ppm range.[8] This indicates a lower electron density at the enolic H atom of these irida-β-diketones when compared to other metalla-β-diketones. Neither the hydride resonance nor the ^{31}P NMR signal is modified on changing the temperature. We therefore believe that the fluxionality of **2** is due to a deprotonation/protonation equilibrium inhibited at low temperature. This equilibrium can be shifted toward the deprotonated or the protonated form by using the appropriate reagent as shown in Scheme 1. The deprotonated form, a diacylhydride species, can be obtained by addition of triethylamine, which gives *trans*-$[IrH(PPh_2(o\text{-}C_6H_4CO))_2(CO)]$ **3** (Scheme 1i). The neutral complex shows IR absorptions at lower frequency than in **2** for both υ(C≡O) and υ(Ir−H), while the hydride, the phosphine, and also the carbonyl resonances appear at slightly lower fields than in the cationic species. In line with the disappearance of the acyl(hydroxycarbene) character, the acyl resonance in **3** appears at higher field, 221 ppm, than in **2** (see Table 2). In the FAB spectrum, the peak due to the protonated form is observed. Addition of stoichiometric amounts of $HBF_4\cdot Et_2O$ to chloroform solutions of **3** allows the formation of the cation in **2** (Scheme 1ii), although attempts to obtain the BF_4 salt of **2** pure were unsuccessful. According to the IR

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(13) Deutsch, P. P.; Eisenberg, R. *J. Am. Chem. Soc.* **1990**, *112*, 714.

(14) Santos, L. L.; Mereiter, K.; Paneque, M.; Slugovc, C.; Carmona, E. *New J. Chem.* **2003**, *27*, 107.

(15) Deutsch, P. P.; Eisenberg, R. *Organometallics* **1990**, *9*, 709.

Table 2. Selected IR Stretching Frequencies (cm^{-1}) and NMR Chemical Shifts (ppm) for Complexes **2** and **3**

complex	υ(Ir−H)	υ(C≡O)	δ(IrH)	δ^{31}P	δ^{13}(C≡O)	δ^{13}(C=O)
2	2128 (s)	2037 (s)	−9.08 (t)	17.9 (s)	169.0 (t)	249.2 (d)
3	2068 (s)	1990 (s)	−8.51 (t)	21.1 (s)	174.5 (br)	220.7 (d)

spectrum, the solid obtained contained always a mixture of [**2**]BF$_4$ and **3**, due to incomplete protonation.

Dimethyl sulfoxide also promotes the immediate deprotonation of **2** to afford **3**. This is not surprising taking into account that dimethyl sulfoxide undergoes protonation to form the [H(DMSO)$_2$]$^+$ cation[16] and that the dissolution of IrCl$_3$ in dimethyl sulfoxide affords [H(DMSO)$_2$]*trans*-[IrCl$_4$(DMSO)$_2$].[17] More unexpectedly, the deprotonation reaction is followed by a slow isomerization (ca. 48 h) of **3** into *cis*-[IrH(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(CO)] **4** as shown in Scheme 1iii. The NMR data indicate the presence of two inequivalent acylphosphine fragments in **4**. The hydride resonance at −8.68 {dd} shows coupling with a trans and with a cis phosphorus atom, while the ^{31}P{^{1}H} NMR spectrum consists of two doublets due to two inequivalent cis phosphorus atoms. The ^{13}C{^{1}H} NMR spectrum shows resonances due to an acyl group trans to phosphorus, an acyl group cis to phosphorus, and the carbonyl group as a triplet due to coupling with two cis phosphorus atoms with equal *J*(P,C) coupling constants. This isomerization reaction of **3** into **4** requires the presence of an acid. Complex **3** remains unaltered in DMSO-d_6 solution, but the addition of stoichiometric amounts of HBF$_4$ promotes its transformation into complex **4**, after ca. 48 h. Most likely, the isomerization reaction involves the formation of hydrogen bonding between the protonated dimethyl sulfoxide and the oxygen of an acyl group. This interaction can be responsible for the opening of the acylphosphine chelate to give the thermodynamic reaction product with the hydride trans to phosphine. It thus appears that the trans isomer **3** is the kinetic product for the carbonyldiacylhydride complex and the thermodynamic product is the cis isomer **4** with only one phosphine group trans to acyl. Consequently with this, attempts to protonate complex **4** in DMSO by addition of HBF$_4$ proved unsuccessful, but the addition of an excess of HBF$_4$ (**4**:HBF$_4$ = 1:3) in dichloromethane leads to its immediate protonation with concomitant isomerization to give **2** as shown in Scheme 1iv. We may conclude that the formation of the corresponding hydridoirida-β-diketone requires both phosphorus atoms and both acyl groups being coplanar.

The molecular structures of compounds **3** and **4** are shown in Figures 1 and 2. Selected bond distances and angles are listed in Table 3. Both complexes are isomers, and **4** crystallizes with two molecules of solvent (chloroform) that form hydrogen bonding with the oxygen atoms of the acyl groups (see Table 3). The geometry about the metal atom is distorted octahedral with four positions occupied by the phosphorus and carbon atoms of two bidentate ligands and the other two position occupied by one hydride ligand and the carbonyl group. While in complex **2** the hydride and the CO group are mutually trans to each other, in complex **3** the hydride is trans to the phosphorus atom of one acylphosphine group and the carbonyl group is trans to the acyl group of the other acylphosphine chelate. The distances comprising the chelate ligands are in the expected ranges.[15,18] The Ir−P distances are equivalent within a given complex. These distances and the Ir−C(carbonyl) distances are also equivalent in both complexes **3** and **4**, in agreement with the similar structural trans influence of the hydride and the acyl ligands.[18b] The Ir−C(acyl) distances are equivalent within a given complex and also in both complexes **3** and **4**. This is also the case for the C=O(acyl) distances. These features suggest a similar structural trans influence of the phosphine and the carbonyl ligands for Ir(III). In **3** and **4**, the Ir−C(acyl) distances, average of 2.09(1) Å in both, are at least 0.04(1) Å longer than the corresponding distances in the hydridoirida-β-diketones **1a** (2.01(1) Å) or **1b** (2.04(1) Å),[6] while the C=O distances in **3** and **4**, average of 1.22(1) Å, are

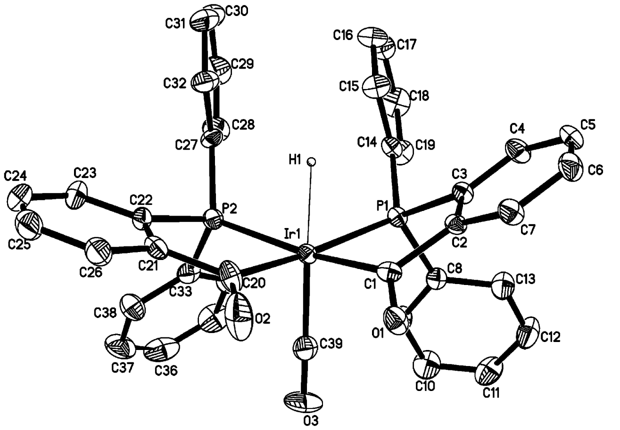

Figure 1. Perspective ORTEP plot of **3**. H atoms, except H1, and the labeling of some C atoms are omitted for clarity. The thermal ellipsoids are at the 30% probability level.

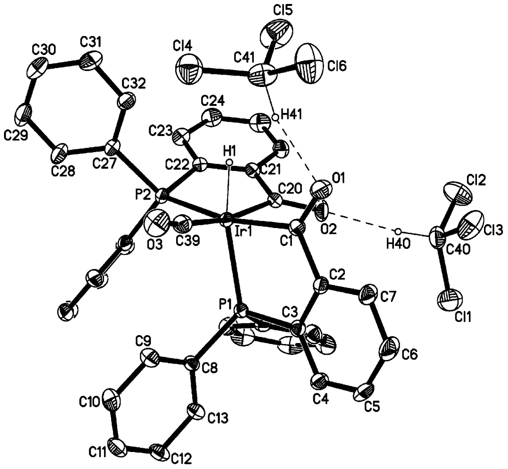

Figure 2. Perspective ORTEP plot of **4**. H atoms, except H1, H40, and H41, and the labeling of some C atoms are omitted for clarity. The thermal ellipsoids are at the 25% probability level.

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(16) Calligaris, M.; Carugo, O. *Coord. Chem. Rev.* **1996**, *153*, 83.

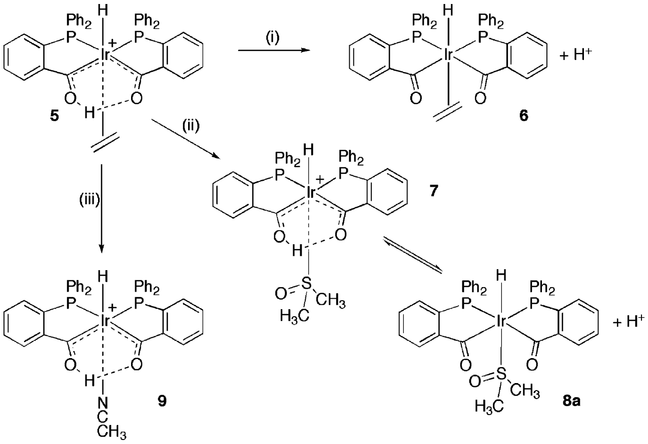
(17) Cartwright, P. S.; Gillard, R. D.; Sillanpaa, E. R. J.; Valkonen, J. *Polyhedron* **1988**, *7*, 2143.

(18) (a) Clark, G. R.; Greene, T. R.; Roper, W. R. *J. Organomet. Chem.* **1985**, *293*, C25. (b) Cleary, B. P.; Eisenberg, R. *J. Am. Chem. Soc.* **1995**, *117*, 3510. (c) Jiménez, M. V.; Sola, E.; Martínez, A. P.; Lahoz, F. J.; Oro, L. A. *Organometallics* **1999**, *18*, 1125. (d) Chan, A. S. C.; Shieh, H. *Inorg. Chim. Acta* **1994**, *218*, 89.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complexes **3**, **4**, and **9** Including the Hydrogen-Bond Geometry

	3	4	9
Ir−P1	2.357(2)	2.354(2)	2.363(2)
Ir−P2	2.349(2)	2.349(2)	2.353(2)
Ir−C1	2.066(7)	2.085(6)	1.97(1)
Ir−C20	2.096(7)	2.087(7)	2.039(9)
Ir−H1	1.8282	1.46(6)	1.5986
Ir−C39	1.932(8)	1.922(8)	
Ir−N1			2.104(7)
C1−O1	1.219(8)	1.205(7)	1.281(9)
C20−O2	1.214(9)	1.240(7)	1.277(10)
C39−O3	1.120(9)	1.132(9)	
C39−N1			1.09(1)
C1−Ir−C20	89.2(3)	87.6(3)	90.0(4)
C1−Ir−P1	81.0(2)	83.3(2)	83.0(3)
C20−Ir−P1	166.6(2)	90.7(2)	172.1(3)
C1−Ir−P2	167.3(2)	167.4(2)	170.9(3)
C20−Ir−P2	83.1(2)	82.8(2)	81.6(3)
P1−Ir−P2	104.9(1)	104.8(1)	105.3(1)
C1−Ir−C39	92.7(3)	88.0(3)	
C1−Ir−N1			93.3(3)
C20−Ir−C39	89.9(3)	167.8(3)	
C20−Ir−N1			92.5(3)
P1−Ir−C39	99.5(2)	100.2(2)	
P1−Ir−N1			91.3(2)
P2−Ir−C39	97.4(2)	99.7(2)	
P2−Ir−N1			90.3(2)
C1−Ir−H1	86.8	85(2)	63.6
C20−Ir−H1	91.5	85(2)	89.9
P1−Ir−H1	79.0	168(2)	84.0
P2−Ir−H1	83.3	86(2)	112.8
C39−Ir−H1	178.4	83(2)	
N1−Ir−H1			156.8
Hydrogen-Bond Geometry			
O1−H2			1.11
O2−H2			1.34
O2----O1			2.420(9)
C40−H40		1.03(7)	
C41−H41		1.03(7)	
C40−O2		3.08(1)	
C41−O1		3.12(1)	
O2····H40		2.08(7)	
O1−H41		2.05(7)	
O1−H2−O2			159.6
C40−H40−O2		161(6)	
C41−H41−O1		158(5)	

Scheme 2 [a]



[a] (i) Et$_3$N in CH$_2$Cl$_2$; (ii) in DMSO; (iii) in CH$_3$CN.

0.04(1) Å shorter than the corresponding distances in **1a** or **1b** (1.27(1) Å) as a consequence of the disappearance of the acyl(hydroxycarbene) character present in the complexes containing a O---H---O moiety. The largest differences between compounds **3** and **4** are found in the maximum deviations of the best least-squares plane for the IrC1O1O2C20 atoms[19] (0.287(7) and 0.490(6) Å) and also in the O1---O2 distances (2.805(8) and 3.431(9) Å) for **3** and **4**, respectively. These differences can be attributed to the different disposition of the bidentate ligands, moreover to the formation of hydrogen bonds in **4**, as shown in Figure 2.

[IrH{(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$H}(OClO$_3$)] **1b** reacts with ethylene with displacement of the perchlorate group to afford the ionic compound [IrH{(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$H}(C$_2$H$_4$)]ClO$_4$ ([**5**]ClO$_4$), containing the cationic ethylene π-complex **5** shown in Scheme 2, as confirmed by NMR measurements. This compound is stable only under ethylene atmosphere, otherwise [**5**]ClO$_4$ loses ethylene readily and several attempts to isolate it led only to mixtures of **1b** and [**5**]ClO$_4$. Complex **5** can be obtained pure and reasonably stable by using noncoordinating anions such as tetrafluoroborate. The reaction of [IrH{(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$H}Cl] **1a** with ethylene in the presence of AgBF$_4$ gives compound [IrH{(PPh$_2$(*o*-C$_6$H$_4$-CO))$_2$H}(C$_2$H$_4$)]BF$_4$ ([**5**]BF$_4$) that has been completely characterized by spectroscopic means and microanalysis. The IR spectrum shows a sharp absorption at 2149 cm^{-1} due to υ(Ir−H) and the υ(C═O) band at 1629 cm^{-1} due to coordinated acyl.

Compound [**5**]BF$_4$ contains two equivalent acylphosphine fragments as shown by the appearance of a singlet at 20.4 ppm in the ^{31}P{^{1}H} NMR spectrum and a doublet at 256.4 ppm (J(P,C) = 85 Hz) in the ^{13}C{^{1}H} NMR spectrum. In the ^{1}H NMR spectrum, a sharp singlet was observed for the ethylene hydrogen atoms at 2.52 ppm, and in the ^{13}C{^{1}H} NMR spectrum the η^2-ethene gave rise to a signal at 70.5 ppm. The alkene rotation is not frozen out for this complex down to 193 K as in other Ir(III) ethylene derivatives.[20] The ^{1}H NMR spectrum shows also a triplet for the hydride resonance at −9.19 ppm with J(P,H) of 15.3 Hz along with the sharp resonance of the O---H---O group at low field, 22.25 ppm, indicating the absence of proton dissociation at room temperature. Compound [**5**]BF$_4$ reacts with triethylamine (Scheme 2i) to give the diacylhydride complex [IrH(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(C$_2$H$_4$)] **6** that shows the υ(Ir−H) absorption at a lower frequency than in the ionic [**5**]BF$_4$. As in the carbonyl case, both the hydride and the phosphine resonances are shifted toward lower fields with respect to the cationic species **5**.

Dissolution of [**5**]BF$_4$ in DMSO-d_6 leads to the displacement of ethylene to give complex [IrH{(PPh$_2$(*o*-C$_6$H$_4$-CO))$_2$H}(DMSO)]BF$_4$ **7** in equilibrium with the deprotonated

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(19) Nardelli, M. *Parst 97*; University of Parma: Parma, Italy, 1997.

(20) (a) Barbaro, P.; Bianchini, C.; Meli, A.; Peruzzini, M.; Vacca, A.; Vizza, F. *Organometallics* **1991**, *10*, 2227. (b) Alvarado, Y.; Boutry, O.; Gutiérrez, E.; Monge, A.; Nicasio, M. C.; Poveda, M. L.; Pérez, P. J.; Ruiz, C.; Bianchini, C.; Carmona, E. *Chem.-Eur. J.* **1997**, *3*, 860. (c) Gutiérrez-Puebla, E.; Monge, A.; Nicasio, M. C.; Pérez, P. J.; Poveda, M. L.; Rey, L.; Ruiz, C.; Carmona, E. *Inorg. Chem.* **1998**, *37*, 4538. (d) Bruin, B.; Peters, T. P. J.; Wilting, J. B. M.; Thewissen, S.; Smits, J. M. M.; Gal, A. W. *Eur. J. Inorg. Chem.* **2002**, 2671.

complex *trans*-[IrH(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(DM*S*O)] **8a** (see Scheme 2ii) as indicated by NMR. The ^{1}H NMR spectrum shows a triplet at −15.34 ppm (*J*(P,H) = 17.2 Hz) due to the hydride, while the O---H---O resonance in the low field region is not observed, and the ^{31}P{^{1}H} NMR spectrum shows a singlet at 23.9 ppm. The addition of dichloromethane and diethyl ether to the DMSO solution led only to the acyl(hydroxycarbene) compound **7**. The ability of the DMSO ligand to displace monoolefins bonded to iridium has been recently reported,[21] and the exchange reaction undergone by complex **5** probably involves initial dissociation of ethylene. **7** can be more easily obtained by the reaction of [IrH{(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$H}Cl] **1a** with DMSO in the presence of AgBF$_4$ (see Experimental Section). The hydride resonance at −15.71 {t} ppm (*J*(P,H) = 16.3 Hz) appears as expected for *S*-coordinated dimethyl sulfoxide trans to the hydride. Only one methyl resonance for the *S*-bound DM*S*O is observed both in the ^{1}H NMR and in the ^{13}C{^{1}H} NMR spectra. The appearance of a sharp singlet at 22.61 ppm in the ^{1}H NMR spectrum indicates the presence of the acyl(hydroxycarbene) group and excludes the formation of hydrogen bonds involving the dimethyl sulfoxide for which the corresponding resonance would be expected at higher field.[22] This is confirmed by the ^{13}C{^{1}H} NMR that shows a resonance at 254.2 ppm.

Complex **7** reacts with triethylamine to give the neutral complex [IrH(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(DM*S*O)] **8** as a mixture of two isomers, *trans*-[IrH(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(DM*S*O)] **8a** and the DM*S*O version of complex **3**, *cis*-[IrH(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(DM*S*O)] **8b**. Compound **8a** shows the proton and phosphorus resonances expected for a hydride ligand trans to sulfur and equivalent phosphorus atoms at lower field than in the parent complex **7**. One methyl resonance for the *S*-bound DM*S*O is observed in the ^{1}H NMR spectrum. Complex **8b** shows resonances in accordance with nonequivalent phosphorus atoms with the hydride ligand trans to phosphorus, and the methyl groups in the *S*-bound DM*S*O give rise to two resonances.

In accordance with the reported ability of acetonitrile to displace ethylene trans to hydride,[23] the dissolution of the ethylene complex [**5**]BF$_4$ in acetonitrile affords [IrH{(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$H}(CH$_3$CN)]BF$_4$ **9**, which can be more easily obtained by the reaction of [IrH{(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$H}Cl] **1a** with acetonitrile in the presence of AgBF$_4$. Complex **9** shows the υ(Ir−H) absorption (2185 cm^{-1}) at higher frequency than in complex **7** (υ(Ir−H), 2160 cm^{-1}) and the hydride resonance (−18.44 {t} ppm) at higher field than in complex **7** (−15.71 {t} ppm). The combination of these data suggests a lower trans influence for acetonitrile than for DM*S*O.[24] A NOESY spectrum of **9** shows a cross-peak between the enolic H atom at 22.62 ppm and the acetonitrile methyl group at 1.56 ppm and supports the structure shown in Scheme 2. Other spectral features for **9** are as expected (see Experimental Section).

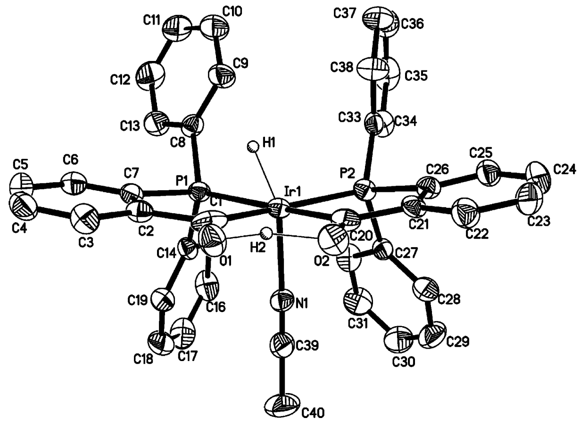

Figure 3. Perspective ORTEP plot of **9**. H atoms, except H1 and H2, and the labeling of some C atoms are omitted for clarity. The thermal ellipsoids are at the 30% probability level.

The acetonitrile complex **9** crystallizes from CHCl$_3$−diethyl ether to afford single crystals suitable for X-ray crystallography. Figure 3 shows the molecular structure of **9**, and selected bond distances and angles are listed in Table 2. The crystal consists of [C$_{40}$H$_{32}$NO$_2$P$_2$Ir]$^+$ mononuclear cations, tetrafluoroborate anions, and solvent molecules. The geometry about the metal atom is distorted octahedral with four positions occupied by P−C of two bidentate ligands bonded between them by a hydrogen bond and the other two positions occupied by the hydride and the acetonitrile ligands mutually trans. The Ir−C bond lengths, 1.98(1) and 2.04(1) Å, are similar to those in previously reported irida-β-diketones,[6] shorter than those in complex **3**, and longer than those reported for carbene iridium compounds such as [CpIr(=CPh$_2$)(P*i*Pr$_3$)] (1.904(5) Å)[25] or [Tp^{Me2}Ir(=CPhR)] (1.914(12) Å).[1b] Both C−O distances, 1.28(1) Å, longer than those in **3**, agree with those reported for other metalla-β-diketones, and the O1---O2 distance 2.420(9) Å is in accordance with a strong hydrogen bridge bond in mononuclear complexes.[6,7,8b] The O---H---O hydrogen bond appears to be slightly unsymmetrical, and the O1−H2−O2 angle (159.6°) is consistent with a nearly linear O---H---O hydrogen bond. The Ir−P distances are as expected, and the Ir−N distance (2.104(7) Å) is similar to those found for complexes in which the acetonitrile and the hydride ligands are mutually trans.[23,26] The iridacycle comprising the acyl(hydroxycarbene) group is essentially planar. The maximum deviation of the best least-squares plane for the IrC1O1O2C20 atoms is 0.0749(1) Å for C1. The dihedral angles between this plane and the best least-squares planes of the IrC1C2C7P1 and IrC20C21C26P2 atoms are 3.9(3)° and 4.3(3)°, respectively. In complex **3**, the corresponding dihedral angles are 19.7(2)° and 11.0(2)°, respectively. These features support some extent of carbenoid character in the carbon atoms bonded to iridium.[27]

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(21) Dorta, R.; Rozenberg, H.; Shimon, L. J. W.; Milstein, D. *Chem.-Eur. J.* **2003**, *9*, 5237.

(22) Buchanan, J.; Hamilton, E. J. M.; Reed, D.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1990**, 677.

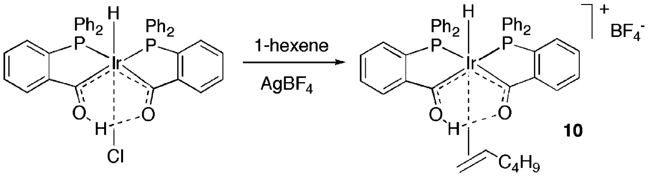
(23) Sola, E.; Navarro, J.; López, J. A.; Lahoz, F. J.; Oro, L. A.; Werner, H. *Organometallics* **1999**, *18*, 3534.

(24) Olgemöller, B.; Beck, W. *Inorg. Chem.* **1983**, *22*, 997.

(25) Ortmann, D. A.; Weberndörfer, B.; Schöneboom, J.; Werner, H. *Organometallics* **1999**, *18*, 952.

(26) (a) He, X. D.; Fernández-Baeza, J.; Chaudret, B.; Folting, K.; Caulton, K. G. *Inorg. Chem.* **1990**, *29*, 5000. (b) Jiménez, M. V.; Caballero, J.; Sola, E.; Lahoz, F. J.; Oro, L. A. *Inorg. Chim. Acta* **2004**, *357*, 1948.

Scheme 3



Terminal olefins such as 1-hexene, with higher steric requirements than ethylene, can also form the corresponding hydridoirida-β-diketone $[IrH\{(PPh_2(o\text{-}C_6H_4CO))_2H\}(C_6H_{12})]BF_4$ **10**, provided an excess of olefin is used if the reaction is to go to completion (Scheme 3). The hydride functionality is responsible for an IR absorption at 2160 cm^{-1} and for the high field ^1H NMR resonance at −10.41 ppm. These data suggest that the hydride ligand is trans to the η^2-coordinated olefin for which the olefinic resonances appear at 2.35 and 3.07 ppm in the ^1H NMR and at 94.5 and 68.8 ppm in the $^{13}C\{^1H\}$ NMR spectrum. A sharp proton resonance at 21.94 ppm confirms the presence of the O---H---O fragment. In this case, the steric effects inhibit the alkene rotation around the Ir−olefin axis, and as a consequence complex **10** contains two inequivalent acylphosphine fragments. In the $^{31}P\{^1H\}$ NMR spectrum, two close doublets at ca. 20 ppm are observed due to two mutually cis phosphines ($J(P,P) = 6$ Hz), and the low field $^{13}C\{^1H\}$ NMR region at ca. 256 ppm also shows two resonances due to two acyl(hydroxycarbene) fragments trans to phosphorus. Consequently, the hydride resonance appears as a doublet of doublet due to coupling to two inequivalent cis phosphorus atoms.

Conclusions

New hydridoirida-β-diketones derived from *o*-(diphenylphosphine)benzaldehyde $[IrH\{(PPh_2(o\text{-}C_6H_4CO))_2H\}(L)]^+$ (L = CO, olefins), with carbenoid character in the acyl groups bonded to iridium, have been prepared. The acyl(hydroxycarbene) moiety requires both phosphorus atoms and both acyl groups being coplanar to be stable. DMSO or CH_3CN displace ethylene to afford new hydridoirida-β-diketones. Deprotonation of the acyl(hydroxycarbene) group allows the isolation of new diacylhydridoiridium(III) derivatives. For the carbonyl complex, the *trans*-$[IrH\{(PPh_2(o\text{-}C_6H_4CO))_2H\}(CO)]$ isomer is the kinetically favored compound and the *cis*-$[IrH\{(PPh_2(o\text{-}C_6H_4CO))_2H\}(CO)]$ is the thermodynamically favored species. A lower trans influence for acetonitrile than for DMSO ligands is observed in these Ir(III) complexes.

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Supporting Information Available: Crystallographic data files of complexes **3**, **4**, and **9** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(27) Sunley, G. J.; Menanteau, P. C.; Adams, H.; Bailey, N. A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1989**, 2415.