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# Synthesis and Reactivity of New Mono- and Dinuclear Hydridoirida-β-diketones – The Formation and Characterization of a Dinuclear Tris-μ-acyliridium(III) Complex

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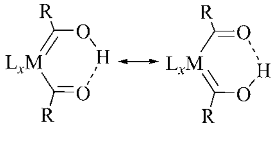
*Dedicated to Professor Victor Riera on the occasion of his retirement*

**Keywords:** Iridium / Hydride ligands / Bridging ligands / P ligands

The hydridoirida-β-diketone $[IrH\{[PPh_2(o\text{-}C_6H_4CO)]_2H\}Cl]$ (**1**) reacts with silver salts of potentially coordinating anions such as tosylate ($^-$OTs) or triflate ($^-$OTf) to afford the mononuclear neutral derivatives $[IrH\{[PPh_2(o\text{-}C_6H_4CO)]_2H\}(X)]$ [X = OTs (**2**), OTf (**3**)]. In acetone solution the triflate anion in **3** is displaced by the solvent to afford the cationic complex $[IrH\{[PPh_2(o\text{-}C_6H_4CO)]_2H\}(acetone)]OTf$ (**4**), which is stable only in acetone solution. The reaction of **1** with halide scavengers containing less coordinating anions such as $PF_6^-$ or $BF_4^-$ results in the formation of cationic compounds $[\{IrH[\{PPh_2(o\text{-}C_6H_4CO)\}_2H]\}_2(\mu\text{-}Cl)]A$ [A = $BF_4$ (**5**), $PF_6$ (**6**)] containing a dinuclear species with a single chlorine atom bridging two hydridoirida-β-diketone fragments. Both fragments are magnetically non-equivalent and the acylphosphane groups in each hydridoirida-β-diketone fragment are chemically equivalent. This species undergoes a fluxional process in solution, with $\Delta H^{\ddagger} = 7.8 \pm 0.4$ kcal mol$^{-1}$ and $\Delta S^{\ddagger} = -10.9 \pm 0.5$ eu. A combination of rotation around the Ir–Cl bonds and variation of the Ir–Cl–Ir angle is suggested to be responsible for the fluxionality. Complex **5** reacts further with $AgBF_4$ to undergo chloride abstraction along with hydrogen loss and deprotonation to give the cationic dinuclear complex $[Ir_2H\{PPh_2(o\text{-}C_6H_4CO)\}\{\mu\text{-}PPh_2(o\text{-}C_6H_4CO)\}_3]BF_4$ (**7**), which contains an acylphosphane chelate along with three acylphosphane bridging ligands and a single hydrido ligand. Bubbling of HCl through an MeOH solution of **7** gives **1**, thus making the loss of hydride, enolic protons and chloride from complex **1** a reversible process. All the complexes were fully characterized spectroscopically. Single-crystal X-ray diffraction analysis was performed on complexes **5** and **7**.

## Introduction

Metalla-β-diketones can be considered as enol tautomers of neutral β-diketones in which the methine group has been substituted by a transition metal organometallic moiety. Therefore, they may also be understood as acyl(hydroxycarbene) complexes that are stabilized by an intramolecular hydrogen bond between the acyl and the hydroxycarbene moiety (see Scheme 1). Hydroxycarbene complexes, for which a tautomeric equilibrium with the acyl hydrides has been reported,[1] have been proposed as important intermediates in CO reduction reactions[2] or in alkene hydrocarbonylation reactions to produce alcohols.[3] Metalla-β-diketones were synthesized for the first time by Lukehart et al. by the protonation of diacylmetalate anions $[L_xM(COR)(COR')]^-$ (M = Mo, W, Mn, Re, Fe, Os).[4] Rhena-β-diketones can be deprotonated by transition metal complexes containing basic ligands to give rhena-β-diketonate derivatives of $Cu^{II}$, $Fe^{II}$, $Cr^{III}$ and $Zn^{II}$.[5] More recently, Steinborn et al. have reported mono- and dinuclear platina-β-diketones obtained by the reaction of hexachloroplatinic acid with alkynes or by the reaction of diacylhydridoplatinum(IV) complexes with $TlPF_6$.[6] Partial deprotonation of the dinuclear derivatives with amines affords platina-β-diketonates of platina-β-diketones.[7] The reaction of $[Ir(Cl)(H)\{PPh_2(o\text{-}C_6H_4CO)\}(cod)]$ (cod = 1,5-cyclooctadiene) with $PPh_2(o\text{-}C_6H_4CHO)$ in protic solvents has allowed the preparation of the first hydridoirida-β-diketone $[IrH\{[PPh_2(o\text{-}C_6H_4CO)]_2H\}Cl]$.[8] Cationic mononuclear hydridoirida-β-



Scheme 1.

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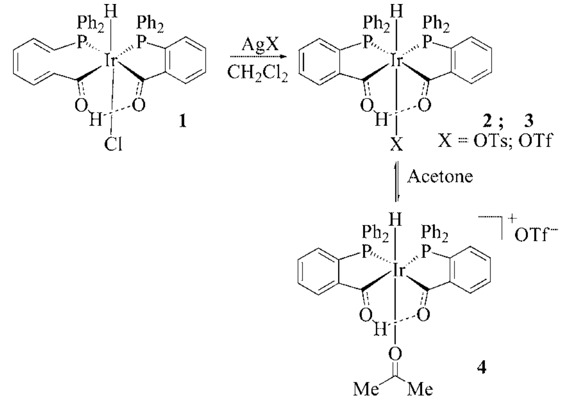
diketones $[IrH\{[PPh_2(o\text{-}C_6H_4CO)]_2H\}(L)]^+$ may undergo reversible deprotonation/protonation reactions, and their reaction with amines affords neutral diacylhydridoiridium(III) derivatives.[9]

We report now on the preparation of new hydridoirida-β-diketones, including novel dinuclear species, and on the deprotonation of the latter to afford a dinuclear tris-μ-acyliridium(III) complex.

## Results and Discussion

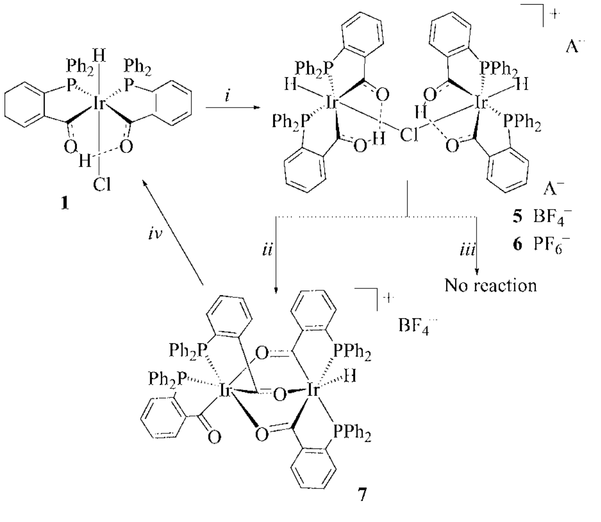
The hydridoirida-β-diketone $[IrH\{[PPh_2(o\text{-}C_6H_4CO)]_2H\}Cl]$ (**1**) reacts with silver salts of potentially coordinating anions such as tosylate ($^-OTs$) or triflate ($^-OTf$) to afford the neutral complexes $[IrH\{[PPh_2(o\text{-}C_6H_4CO)]_2H\}(X)]$ [X = OTs (**2**), OTf (**3**)] with loss of AgCl, as shown in Scheme 2. The IR spectrum of **3** indicates the presence of the coordinated triflate anion, as shown by the presence of a ν(SO) absorption at 1317 $cm^{-1}$, which is shifted to higher wavenumbers with respect to the free anion (1270 $cm^{-1}$) upon coordination, as expected.[10] The IR spectrum of **2** contains a ν(SO) absorption at 1259 $cm^{-1}$, which is also shifted towards higher wavenumbers with respect to the silver tosylate (1205 $cm^{-1}$).[11] The FAB mass spectra show the corresponding $[M - X]^+$ peak, as expected for mononuclear complexes. Both the ν(Ir–H) absorptions (2224 $cm^{-1}$ for **2** and 2264 $cm^{-1}$ for **3**) at rather high wavenumber and the hydride resonances ($\delta$ = –24.24 ppm for **2** and –25.89 ppm for **3**) at rather high field are in accordance with a hydrido ligand being *trans* to the bonded oxygen atom of the anion.[8] The σ-donor strength of O-coordinated anions is among the smallest and this is reflected in the *trans* effect.[12] The NMR spectroscopic data for both **2** and **3** indicate the presence of two equivalent acylphosphane fragments. The $^{31}P\{^1H\}$ NMR spectra show singlets at $\delta \approx 30$ ppm and the $^{13}C\{^1H\}$ NMR spectrum of **2** shows a doublet at $\delta$ = 256.9 ppm, in the range expected for irida-β-diketones with acyl(hydroxycarbene) character, with a large $J_{P,C}$ coupling constant of 102 Hz due to the acyl groups being *trans* to the phosphorus atoms. The $^1H$ NMR spectra show the hydride resonances as triplets due to a $J_{P,H}$ coupling of about 12 Hz, which agrees with the hydride being *cis* to both phosphane ligands, and sharp, low-field singlets at $\delta$ = 22.72 ppm for **2** and 22.69 ppm for **3**, which support the presence of fairly strong O···H···O hydrogen bonds and the existence of irida-β-diketones containing a formally tetradentate PCCP ligand.[8,9]



Scheme 2.

Complex **2** behaves as nonelectrolyte in acetone solution, whereas acetone solutions of **3** show conductivity values expected for 1:1 electrolytes.[13] This indicates that in acetone solution the tosylate group remains bonded to the iridium ion while the triflate anion is easily displaced by the solvent to afford the cationic complex $[IrH\{[PPh_2(o\text{-}C_6H_4CO)]_2H\}(acetone)]OTf$ (**4**), as shown in Scheme 2. To confirm this assumption, we recorded the NMR spectra of both complexes in $[D_6]$acetone solution. The $^1H$ NMR spectrum of **2** in $[D_6]$acetone is almost the same as that in $CDCl_3$, with the hydride resonance at $\delta$ = –24.03 (t, $J_{P,H}$ = 13.25 Hz) ppm, while the $^1H$ NMR spectrum of **3** shows two hydride resonances in a 6:1 ratio according to the integrals. The most abundant signal – that of the hydride at $\delta$ = –24.59 (t, $J_{P,H}$ = 12.80 Hz) ppm – is due to **4** and appears at lower field (ca. 1 ppm) than that of **3**, which appears at $\delta$ = –25.74 (t, $J_{P,H}$ = 13.25 Hz) ppm in $CDCl_3$. Attempts to obtain the acetone complex **4** proved unsuccessful and only resulted in the isolation of complex **3**.

The reaction of $[IrH\{[PPh_2(o\text{-}C_6H_4CO)]_2H\}Cl]$ (**1**) with halide scavengers containing noncoordinating anions such as $Et_3OPF_6$, $Et_3OBF_4$ or $AgBF_4$ and using Ir/scavenger ratios of 2:1 results in the abstraction of only one half of the chlorine atoms in the starting material and the formation of the compounds $[\{IrH[\{PPh_2(o\text{-}C_6H_4CO)\}_2H]\}_2(\mu\text{-}Cl)]A$ [A = $BF_4$ (**5**), $PF_6$ (**6**)], which contain a cationic dinuclear species with a single chlorine atom bridging two hydridoirida-β-diketone fragments (see *i* in Scheme 3). The spectroscopic data for the cation in compounds **5** and **6** are the same. Compounds **5** and **6** show a ν(Ir–H) absorption and a hydride resonance that agree with a hydride ligand being *trans* to a chlorine atom, and a sharp, low-field singlet at $\delta$ = 22.66 ppm that supports the presence of an O···H···O



Scheme 3. *i*: $AgBF_4$, $Et_3OBF_4$ or $Et_3OPF_6$ in $CH_2Cl_2$; *ii*: $AgBF_4$ in $CH_2Cl_2$; *iii*: $Et_3OBF_4$ or $Et_3OPF_6$ in $CH_2Cl_2$; *iv*: HCl in MeOH.

fragment. They behave as 1:1 electrolytes in acetone solution and the FAB spectrum of **6** shows the $[M]^+$ peak at *m*/*z* = 1581, as expected for such a dinuclear species.

In order to ascertain the structure shown in Scheme 3, a single-crystal X-ray diffraction study of compound **5** was undertaken. Selected bond lengths and angles, including the enolic hydrogen bond, are listed in Table 1. The crystal structure consists of discrete, cationic dinuclear units formed by pseudo-octahedral Ir moieties sharing the position occupied by the chloro ligand and $BF_4^-$ anions. An ORTEP view of the cation is given in Figure 1. Both bridging Ir–Cl distances in **5** are equal within experimental error and are, as expected, significantly longer [2.539(3) Å] than the terminal Ir–Cl distance in **1** [2.485(3) Å].[8] As far as we are aware, there is only one precedent of a dinuclear iridium complex containing a single chlorine bridge, which is *trans* to an $SiR_2R'$ group.[14] The Ir–Cl distances in **5** are shorter than those found in this previously reported complex and this difference may reflect the expected stronger structural *trans* influence of $SiR_3$ groups than of hydrido ligands.[15] The coordination around both Ir atoms is pseudo-octahedral with distortions of the type usually observed in hydrido complexes (maximal deviation from ideal angles of 19° and 16° for Ir1 and Ir2, respectively). The Ir1–Ir2 distance (4.609 Å) and the Ir1–Cl1–Ir2 angle [130.3(1)°] exclude any Ir–Ir interaction. This angle is similar to those reported for related octahedral rhodium [138.15(7)°] or molybdenum [134.0(1)°] complexes containing a single chlorine bridge between two metal atoms.[16] The best least-squares equatorial planes (P1, P2, C20, C1) and (P3, P4, C39, C58) of the Ir atoms form a dihedral angle of 54.1(2)°, in accordance with the Ir1–Cl1–Ir2 angle. There are some differences between both moieties. For example, the average Ir–P distances are slightly longer [by 0.023(3) Å] in the Ir1 moiety and the relative disposition of the pseudo-octahedra is eclipsed with a slight torsion angle of 26.71°. These facts mean a breaking of the $C_2$ symmetry around the chlorine atom for the whole structure and the twofold axis is only

Table 1. Selected bond lengths [Å] and angles [°] for Complex **5**.

| | | | |
|---|---|---|---|
| Ir1–P1 | 2.372(3) | Ir2–P3 | 2.336(3) |
| Ir1–P2 | 2.364(3) | Ir2–P4 | 2.354(3) |
| Ir1–C1 | 2.01(1) | Ir2–C58 | 2.01(1) |
| Ir1–C20 | 2.05(1) | Ir2–C39 | 2.03(1) |
| Ir1–H1A | 1.417 | Ir2–H1B | 1.420 |
| Ir1–Cl(1) | 2.535(3) | Ir2–Cl(1) | 2.544(3) |
| C1–O1 | 1.31(1) | C39–O3 | 1.27(1) |
| C20–O2 | 1.28(1) | C58–O4 | 1.27(1) |
| O2–H2A | 1.16 | O3–H2B | 1.19 |
| O1–H2A | 1.27 | O4–H2B | 1.33 |
| O2····O1 | 2.39(1) | O4····O3 | 2.42(1) |
| C1–Ir1–C20 | 91.7(5) | C39–Ir2–C58 | 90.3(5) |
| C1–Ir1–P1 | 81.5(4) | C39–Ir2–P3 | 83.7(4) |
| C20–Ir1–P1 | 168.8(3) | C58–Ir2–P3 | 173.9(4) |
| C1–Ir1–P2 | 172.8(4) | C39–Ir2–P4 | 164.3(4) |
| C20–Ir1–P2 | 81.6(4) | C58–Ir2–P4 | 82.2(4) |
| P1–Ir1–P2 | 104.7(1) | P3–Ir2–P4 | 103.6(1) |
| C1–Ir1–Cl(1) | 89.0(3) | C39–Ir2–Cl(1) | 98.9(3) |
| C20–Ir1–Cl(1) | 92.4(3) | C58–Ir2–Cl(1) | 88.7(3) |
| P1–Ir1–Cl(1) | 96.4(1) | P3–Ir2–Cl(1) | 92.8(1) |
| P2–Ir1–Cl(1) | 94.0(1) | P4–Ir2–Cl(1) | 94.7(1) |
| C1–Ir1–H1A | 104.6 | C39–Ir2–H1B | 77.0 |
| C20–Ir1–H1A | 83.1 | C58–Ir2–H1B | 102.0 |
| P1–Ir1–H1A | 90.0 | P3–Ir2–H1B | 76.1 |
| P2–Ir1–H1A | 71.9 | P4–Ir2–H1B | 91.1 |
| Cl(1)–Ir1–H1A | 165.7 | Cl(1)–Ir2–H1B | 168.4 |
| O2–H2A–O1 | 159.0 | O3–H2B–O4 | 147.4 |
| Ir1–Cl(1)–Ir2 | 130.3(1) | | |

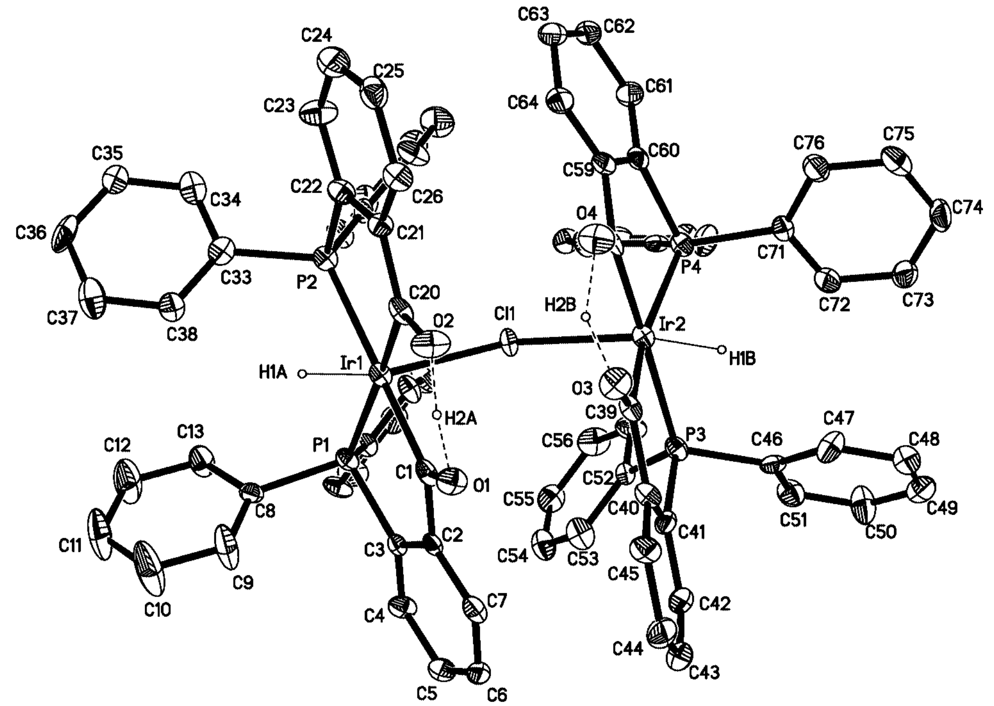


Figure 1. ORTEP view of the cation in **5** showing the atomic numbering (20% probability ellipsoids) and the intramolecular hydrogen bonds. The hydrogen atoms, except for the four shown, and the labels of some carbon atoms have been omitted for clarity.

kept for the Ir cores. The C=O distances, which are in the range 1.27–1.31 Å, are similar to those found in monomeric irida-β-diketones. The O···O distances and O–H–O angles are in accordance with a strong enolic character for the hydrogen bond and agree with those reported for other irida-β-diketones.[8,9]

In keeping with the crystal structure, the $^{31}P\{^1H\}$ NMR spectra of **5** and **6** show two singlets at $\delta$ = 30.7 and 18.3 ppm, respectively, at 203 K, and in the $^{13}C\{^1H\}$ NMR spectra two doublets at $\delta$ = 257.6 ($J_{P,C}$ = 101 Hz) and 255.6 ppm ($J_{P,C}$ = 103 Hz) are observed. The $^1H$ NMR spectra contain a triplet at $\delta$ = –23.17 ($J_{P,H}$ = 14.6) ppm and a singlet at $\delta$ = 22.66 ppm. Such a pattern is consistent with the nonequivalence of the hydridoirida-β-diketone fragments connected through the chlorine bridge, the equivalence of the acylphosphane groups in each hydridoirida-β-diketone fragment, and the NMR parameters of the hydride ions and of the enolic protons of both fragments being equal. Inspection of the $^{31}P\{^1H\}$ NMR spectra at various temperatures shows that on raising the temperature the singlets broaden and coalesce at 253 K, giving rise to a broad resonance centered at $\delta$ = 25 ppm at room temperature (see Figure 2). On the other hand, at room temperature the $^{13}C\{^1H\}$ NMR spectra show only a doublet at $\delta$ = 256.5 ($J_{P,C}$ = 101 Hz) ppm due to the bonded acyl groups. The $^1H$ NMR spectra remain unaltered in the whole temperature range. From line-shape analysis[17] of the variable-temperature $^{31}P\{^1H\}$ NMR spectra of complex **5**, the activation parameters $\Delta H^{\ddagger}$ = 7.8 ± 0.4 kcal mol$^{-1}$ and $\Delta S^{\ddagger}$ = –10.9 ± 0.5 cal K$^{-1}$ mol$^{-1}$ have been determined. The entropy of activation is indicative of an intramolecular rearrangement process.[18] A combination of rotation around the Ir–Cl bonds, which is restricted at low temperatures due to the presence of the phenyl groups, and variation of the Ir–Cl–Ir angle may account for the observed fluxional behavior.

Complex **5** reacts further with $AgBF_4$ to give complex **7**, which contains three acylphosphane bridging groups (see *ii* in Scheme 3). Compound **7** shows an IR stretch at 1628 cm$^{-1}$ due to the terminal acyl group and a strong stretch at 1525 cm$^{-1}$ assigned to the bridging acyl groups. It behaves as 1:1 electrolyte in acetone solution and the FAB spectrum shows the $[M]^+$ peak at *m*/*z* = 1543, as expected for such a dinuclear species. At 223 K, the NMR spectra of **7** are consistent with the structure shown in Scheme 3. The $^1H$ NMR spectrum shows only one resonance at high field ($\delta$ = –23.24 ppm) as a doublet of doublets, with a $J_{P,H}$ coupling of about 18 Hz, due to the presence of one hydrido ligand *cis* to two nonequivalent phosphorus atoms. The formation of three bridging acyl groups breaks the equivalence of the acylphosphane fragments present in the starting material **5**. The $^{31}P\{^1H\}$ NMR spectrum consists of two sets of doublets due to the presence of four nonequivalent acylphosphane fragments, two per iridium atom, and the $J_{P,P}$ coupling constants agree with both phosphorus atoms bonded to the same iridium atom being mutually *cis*. The $^{13}C\{^1H\}$ NMR spectrum contains a singlet at $\delta$ = 209.1 ppm due to the terminal acyl group and three resonances at $\delta$ = 266.5 (d), 264.8 (d), and 257.5 (d) ppm, respectively, with high $J_{P,C}$ coupling constants of about 95 Hz, due to three acyl groups *trans* to phosphorus atoms. The rather low field of the latter suggests the bridging nature and significant carbene-like character for all three acyl groups.[19–21] Inspection of the NMR spectra at variable temperature shows that on raising the temperature the doublet of doublets due to the hydrido ligand collapses into a triplet at $\delta$ = –23.23 ($J_{P,H}$ = 18.3 Hz) ppm. The $^{31}P\{^1H\}$ resonances at lower field ($\delta$ = 23 and 21 ppm) show a marked chemical shift temperature dependence such that $\Delta\delta$ decreases as the temperature increases and the AX system observed at low temperature becomes an AB system centered at $\delta$ = 22.3 ppm. The two chemical shifts coincide at room temperature, and above this temperature they exchange position. This behavior has also been reported for monomeric Ir$^{III}$ complexes.[22] Over the whole temperature range, the corresponding $J_{P,P}$ value, the $^{31}P\{^1H\}$ resonances at higher field, and the $^{13}C\{^1H\}$ resonances remain unchanged. A $\{^1H,^{31}P\}$ HSQC experiment at room temperature shows that the hydrido ligand is coupled to the $^{31}P$ AB system at $\delta$ = 22 ppm.

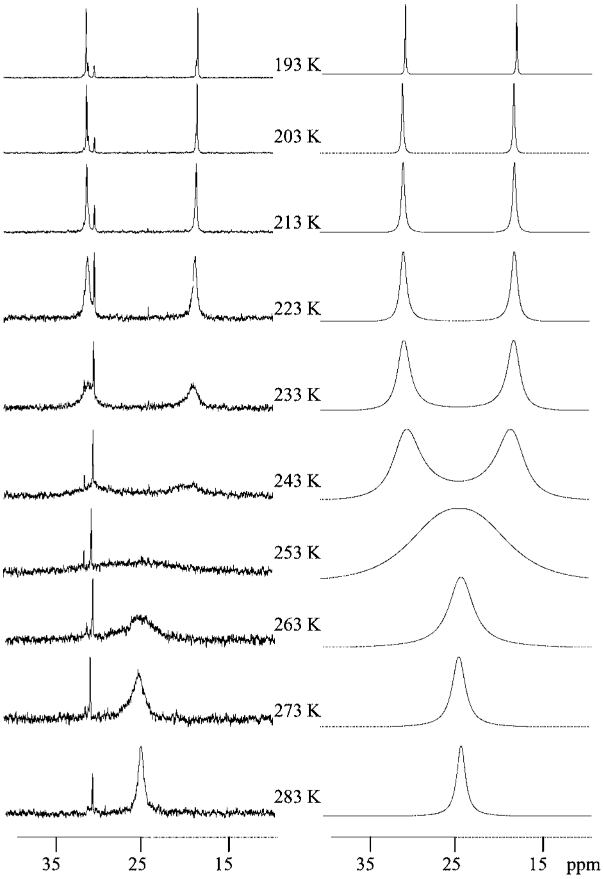


Figure 2. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of **5**; experimental in $CD_2Cl_2$ (left) and calculated (right).

Acyl groups are well known as bridging ligands towards transition metals, although their behavior as such in iridium homodinuclear complexes is scarce,[21] and the acylphosphane chelating ligand *o*-$PPh_2(C_6H_4CO)$ has been reported to behave as a bridging acyl group only in ruthenium or osmium clusters.[23] We have succeeded in isolating complex **7** as single crystals suitable for X-ray diffraction. To the best of our knowledge no structural report on dinuclear transition metal complexes with three bridging acyl groups has been published, although a crystallographic study of a triacetylrhenate complex of boron has been reported.[24] The crystal structure of **7** shows the presence of dinuclear cations and $BF_4^-$ anions packed within normal van der Waals interaction distances. Two crystallographically independent cations and anions were identified in the structural determination, namely A and B. No significant differences are observed in the molecular geometries of both. Selected bond lengths and angles are listed in Table 2, and Figure 3 shows a molecular drawing of the cation A. The dinuclear cation consists of two pseudo-octahedral iridium(III) moieties, assuming that the hydrido ligand occupies the sixth coordination site on Ir1A, with three bridging acyl groups. Two of the corresponding carbon atoms are bonded to the iridium atom coordinated to the hydrido ligand such that the coordination around Ir1 is similar to that of the parent hydridoirida-β-diketone **5**. The hydrido ligand is *trans* to the oxygen atom in **7** instead of to the chlorine atom in **5** and the two oxygen atoms are bonded to the iridium atom in **7** instead of to a proton in **5**. Ir2 is bonded to two oxygen atoms and one carbon atom of the bridging acyl groups and six-coordination is attained with two phosphane groups and one terminal acyl group. The Ir–P distances in the Ir1A moiety and the Ir2A–P3A distance are equivalent [average of 2.354(4) Å] and longer than the Ir2A–P4A distance of 2.242(4) Å as a consequence of the weaker structural *trans* influence of the oxygen atom *trans* to P4 than that of an acyl carbon atom *trans* to P1, P2, and P3. The Ir–O distances [2.23(1), 2.19(1), and 2.12(1) Å for Ir1A–O4A, Ir2A–O1A, and Ir2A–O2A, respectively] reflect the *trans* influence being strongest for the hydrido ligand, similar or slightly weaker for the acyl carbon atom, and weaker for the phosphorus atom. Bridging acyl groups can be described by acyl↔oxycarbene resonance structures and this is reflected by shorter M–C and longer C–O bond lengths than in terminal acyl ligands.[19–21] In spite of the oxycarbene character of the bridging acyl groups suggested by $^{13}C$ NMR spectroscopy, the Ir–C and C–O distances for the bridging groups in complex **7** [average of 2.03(2) and 1.23(2) Å, respectively] are similar to the Ir2A–C39A [1.97(2) Å] and the C39A–O3A [1.26(2) Å] distances of the terminal acyl ligand. These fea-

Table 2. Selected bond lengths [Å] and angles [°] for complex **7**.

| | | | |
|---|---|---|---|
| Ir1A–P1A | 2.345(4) | Ir2A–P3A | 2.363(4) |
| Ir1A–P2A | 2.353(4) | Ir2A–P4A | 2.242(4) |
| Ir1A–O4A | 2.23(1) | Ir2A–O1A | 2.185(8) |
| | | Ir2A–O2A | 2.123(8) |
| Ir1A–C1A | 2.03(1) | Ir2A–C39A | 1.97(2) |
| Ir1A–C20A | 2.02(1) | Ir2A–C58A | 2.05(2) |
| C1A–O1A | 1.23(1) | C39A–O3A | 1.26(2) |
| C20A–O2A | 1.25(1) | C58A–O4A | 1.21(2) |
| C1A–Ir1A–P1A | 80.9(4) | C39A–Ir2A–P3A | 83.2(5) |
| C1A–Ir1A–P2A | 167.6(4) | C39A–Ir2A–P4A | 93.2(5) |
| C20A–Ir1A–P2A | 80.2(4) | P4A–Ir2A–P3A | 102.4(2) |
| C20A–Ir1A–P1A | 172.3(4) | O1A–Ir2A–P4A | 94.0(2) |
| C20A–Ir1A–C1A | 91.7(6) | C58A–Ir2A–P3A | 173.2(4) |
| P1A–Ir1A–P2A | 106.7(1) | C58A–Ir2A–P4A | 80.6(4) |
| O1A–C1A–Ir1A | 128(1) | O2A–Ir2A–P4A | 172.5(3) |
| O2A–C20A–Ir1A | 127(1) | O2A–Ir2A–O1A | 86.0(3) |
| C58A–O4A–Ir1A | 121(1) | C1A–O1A–Ir2A | 120.1(9) |
| C39A–Ir2A–O1A | 172.9(5) | C20A–O2A–Ir2A | 124.3(8) |
| C39A–Ir2A–O2A | 86.9(5) | O4A–C58A–Ir2A | 128(1) |

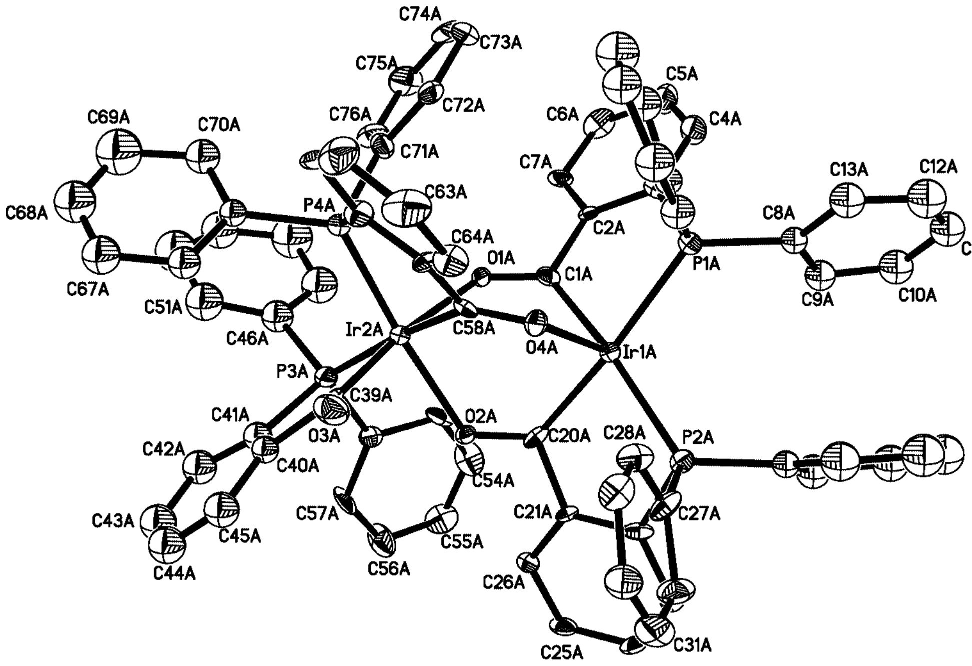


Figure 3. ORTEP view of the cation A in complex **7** showing the atomic numbering (20% probability ellipsoids). The hydrogen atoms and the labels of some carbon atoms have been omitted for clarity.

tures may be related to the fact that the terminal acyl ligand is *trans* to the oxygen atom, which has a weak *trans* influence, while the carbon atoms of the bridging ligands are *trans* to the phosphorus atoms, and/or to the acyl resonance structure being a stronger contributor than the oxycarbene resonance structure to the ground-state structure, as suggested for related iridium(III) complexes.[22]

The reaction of **5** with AgBF$_4$ to give **7** is a complex transformation and its mechanism is not yet totally clear. Complex **5** contains two hydrido ligands and also two enolic protons along with a chlorine atom, while complex **7** contains only one hydrido ligand; this means release of one Cl and three H atoms. Attempts to abstract the chloride ion from complexes **5** or **6** by using Et$_3$OBF$_4$ or Et$_3$OPF$_6$ proved unsuccessful (see *iii* in Scheme 3) and this indicates that the silver salt promotes a reaction path that is not available for other halide scavengers. It is known that metathesis reactions of silver salts may lead to the formation of different adducts that can involve silver coordination to the iridium atom,[25] or formation of a halide bridge between both metal atoms.[26] In our case, replacement of the enolic protons by silver ions, similar to that observed in pyrazolyliridium complexes,[27] can also be considered. Cationic acyl(hydroxycarbene)platinum(II) complexes can be obtained by the reaction of diacylhalohydridoplatinum(IV) complexes with TlPF$_6$ and may involve an intermolecular deprotonation/protonation reaction.[28] We believe that the silver salt is responsible for the abstraction of the chloride ion and one proton, while evolution of H$_2$, formed by combination of one hydride ion and one proton, occurs.

Bubbling of HCl through an MeOH solution of **7** gives **1** (see *iv* in Scheme 3). This result shows that the loss of hydrido ligands, enolic protons, and chloride ions in complex **1** can be reversed; this observation has potential interest in studies directed toward catalytic ionic hydrogenation.[29]

## Conclusions

Neutral, mononuclear hydridoirida-β-diketones containing labile anions have been prepared that can be used to afford mononuclear, cationic hydridoirida-β-diketones. Fluxional, dinuclear, cationic hydridoirida-β-diketones containing a single chloride bridge can be obtained upon treatment with a halide abstractor. Silver salts may afford an asymmetric, dinuclear iridium complex with three acylphosphane bridging ligands. The starting material can be recovered by addition of HCl. The loss and recovery of hydride ions and protons could be relevant to studies of catalytic processes such as ionic hydrogenation.

## Experimental Section

**General Procedures:** The preparation of the metal complexes was carried out at room temperature under nitrogen by using standard Schlenk techniques. [IrH{[PPh$_2$(*o*-C$_6$H$_4$CO)]$_2$H}Cl] (**1**) was prepared as reported previously.[8] Microanalysis were carried out with a Leco CHNS-932 microanalyser. Conductivities were measured in acetone solution with a Metrohm 712 conductimeter. IR spectra were recorded with a Nicolet FTIR 510 spectrophotometer in the range 4000–400 cm$^{-1}$ using KBr pellets. NMR spectra were recorded with Bruker Avance DPX 300 or Bruker Avance 500 spectrometers. $^1$H and $^{13}$C{$^1$H} (TMS internal standard), $^{31}$P{$^1$H} (H$_3$PO$_4$ external standard) and 2D spectra were measured for CDCl$_3$, CD$_2$Cl$_2$, or [D$_6$]acetone solutions. Mass spectra were recorded with a VG Autospec, by the liquid secondary ion (LSI) technique using nitrobenzyl alcohol as matrix and a cesium gun (Universidad de Zaragoza).

**Preparation of [IrH{[PPh$_2$(*o*-C$_6$H$_4$CO)]$_2$H}(OTs)] (2):** AgOTs (42 mg, 0.150 mmol) was added to a dichloromethane solution of **1** (60 mg, 0.075 mmol). After stirring for 24 h, the silver salts were filtered off. Addition of diethyl ether to the solution gave a yellow precipitate, which was filtered off, washed with diethyl ether, and vacuum-dried (yield: 50 mg, 70%). IR (KBr): ṽ = 2224 (w) [ν(IrH)], 1632(s) [ν(C=O)], 1259(s) [ν(SO)] cm$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ = –24.24 (t, $J_{P,H}$ = 12.24 Hz, 1 H, HIr), 2.19 (s, 3 H, CH$_3$), 22.72 (s, 1 H, OHO) ppm. $^{13}$C{$^1$H} NMR (CDCl$_3$): $\delta$ = 256.9 (d, $J_{P,C}$ = 102 Hz, CO), 21.2 (s, CH$_3$) ppm. $^{31}$P{$^1$H} NMR (CDCl$_3$): $\delta$ = 29.9 (s) ppm. FAB MS: calcd. for C$_{45}$H$_{37}$IrO$_5$P$_2$S 944, found 773 [M – OTs]$^+$. C$_{45}$H$_{37}$IrO$_5$P$_2$S·0.25CH$_2$Cl$_2$ (965.25): calcd. C 56.31, H 3.92, S 3.32; found C 56.18, H 3.89, S 3.44.

**Preparation of [IrH{[PPh$_2$(*o*-C$_6$H$_4$CO)]$_2$H}(OTf)] (3):** AgOTf (38 mg, 0.150 mmol) was added to a dichloromethane solution of **1** (60 mg, 0.075 mmol). After stirring for 30 min, the silver salts were filtered off. Addition of diethyl ether to the solution gave a yellow precipitate, which was filtered off, washed with diethyl ether, and vacuum-dried (yield: 47 mg, 68%). IR (KBr): ṽ = 2264 (w) [ν(IrH)], 1628 (s) [ν(C=O)], 1317 (s) [ν(SO)] cm$^{-1}$. $\Lambda_M$ = 116 Ω$^{-1}$cm$^2$mol$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ = –25.89 (t, $J_{P,H}$ = 12.86 Hz, 1 H, HIr), 22.69 (s, 1 H, OHO) ppm. $^{31}$P{$^1$H} NMR (CDCl$_3$): $\delta$ = 31.21 (s) ppm. FAB MS: calcd. for C$_{39}$H$_{30}$F$_3$IrO$_5$P$_2$S 922; found 773 [M – OTf]$^+$. C$_{39}$H$_{30}$F$_3$IrO$_5$P$_2$S (921.89): calcd. C 50.81, H 3.28, S 3.48; found C 50.74, H 3.57, S 3.45.

**Preparation of [{IrH[{PPh$_2$(*o*-C$_6$H$_4$CO)}$_2$H]}$_2$(μ-Cl)]A [A = BF$_4$ (5), PF$_6$ (6)]:** Et$_3$OPF$_6$ (9.42 mg, 0.038 mmol) or Et$_3$OBF$_4$ (7.22 mg, 0.038 mmol) was added to a dichloromethane solution of **1** (60 mg, 0.075 mmol). After stirring for 60 min, addition of diethyl ether to the solution gave a yellow precipitate, which was filtered off, washed with diethyl ether, and vacuum-dried. IR (KBr): ṽ = 2221 (m) [ν(IrH)], 1629 (s) [ν(C=O)] cm$^{-1}$. $^1$H NMR (CD$_2$Cl$_2$, 203 K): $\delta$ = –23.17 (t, $J_{P,H}$ = 14.2 Hz, 1 H, HIr), 22.66 (s, 1 H, OHO) ppm. $^{13}$C{$^1$H} NMR (CD$_2$Cl$_2$, 203 K): $\delta$ = 257.6 (d, $J_{P,C}$ = 101 Hz, CO), 255.6 (d, $J_{P,C}$ = 103 Hz, CO) ppm. $^{31}$P{$^1$H} NMR (CD$_2$Cl$_2$, 203 K): $\delta$ = 30.7 (s), 18.3 (s) ppm. FAB MS: calcd. for C$_{76}$H$_{60}$ClO$_4$P$_4$Ir$_2$ 1581; found 1581 [M]$^+$. **Data for 5:** Yield: 42 mg (68%). $\Lambda_M$ = 147 Ω$^{-1}$cm$^2$mol$^{-1}$. C$_{76}$H$_{60}$BClF$_4$Ir$_2$O$_4$P$_4$ (1667.9): calcd. C 54.73, H 3.63; found C 54.61, H 3.57. **Data for 6:** Yield: 48 mg (73%). $\Lambda_M$ = 179 Ω$^{-1}$cm$^2$mol$^{-1}$. C$_{76}$H$_{60}$ClF$_6$Ir$_2$O$_4$P$_5$·0.5CH$_2$Cl$_2$ (1768.5): calcd. C 51.96, H 3.48; found C 52.03, H 3.23.

**Preparation of [Ir$_2$H{PPh$_2$(*o*-C$_6$H$_4$CO)}{μ-PPh$_2$(*o*-C$_6$H$_4$CO)}$_3$]BF$_4$ (7):** To a dichloromethane solution of **5** (125 mg, 0.075 mmol) was added AgBF$_4$ (29.1 mg, 0.15 mmol). After stirring for 30 min, the silver salts were filtered. Addition of diethyl ether to the solution gave a yellow precipitate that was filtered off, washed with diethyl ether and vacuum-dried (yield: 68 mg, 53%). IR (KBr): ṽ = 2189 (w), [ν(IrH)], 1628 (s), 1525 (s) [ν(C=O)] cm$^{-1}$. $\Lambda_M$ = 152 Ω$^{-1}$cm$^2$mol$^{-1}$. $^1$H NMR (CDCl$_3$, 223 K): $\delta$ = –23.24 (dd, $J_{P,H}$ = 19.2 and 18.3 Hz, 1 H, HIr) ppm. $^{31}$P{$^1$H} NMR (CDCl$_3$, 223 K): $\delta$ = 23.6 and 21.2 (d, $J_{P,P}$ = 12 Hz), 20.1 and 14.2 (d, $J_{P,P}$

Table 3. Crystal and refinement fata for **5** and **7**.

| | **5** | **7** |
|---|---|---|
| Empirical formula | $[C_{76}H_{60}Cl_1O_4P_4Ir_2]BF_4 \cdot 1/2CH_2Cl_2$ | $[C_{76}H_{56}F_3O_4P_4Ir_2]BF_4$ |
| $M_r$ | 1710.24 | 1628.3 |
| Crystal system | monoclinic | monoclinic |
| Space group | $P2_1/c$ | $P2_1/n$ |
| $a$ [Å] | 14.3279(7) | 15.583(1) |
| $b$ [Å] | 36.606(2) | 36.688(2) |
| $c$ [Å] | 13.235(7) | 23.299(2) |
| $\beta$ [°] | 97.062(1) | 94.954(2) |
| $V$ [Å$^3$] | 6888.6(6) | 13271(2) |
| $Z$ | 4 | 8 |
| $D_{calcd.}$ [g cm$^{-3}$] | 1.649 | 1.630 |
| $\mu$ [mm$^{-1}$] | 4.091 | 4.165 |
| $F$(000) | 3364 | 6392 |
| $\theta$ [°] | 1.11–25.0 | 1.04–25.0 |
| Data collected | (–17, –42, –14) to (15, 43, 15) | (–18, –40, –26) to (18, 43, 27) |
| No. of reflns. collected | 36113 | 102296 |
| No. of ind. reflns. | 12105 ($R_{int}$ = 0.1195) | 23299 ($R_{int}$ = 0.1700) |
| Completeness to $\theta$ | 99.8% | 99.6% |
| Data/restraints/parameters | 12105/6/616 | 23299/8/1279 |
| $R$[a] [$I > 2\sigma(I)$] | 0.0585 (6212 obsd. reflect.) | 0.0553 (8848 obsd. reflect.) |
| $R_{wF}$[b] (all data) | 0.16000 | 0.1306 |

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

= 8 Hz) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 223 K): $\delta$ = 266.5 (d, $J_{P,C}$ = 91 Hz, CO), 264.5 (d, $J_{P,C}$ = 89 Hz, CO), 257.5 (d, $J_{P,C}$ = 101 Hz, CO) 209.1 (s, CO) ppm. FAB MS: calcd. for $C_{76}H_{57}O_4P_4Ir_2$ 1543; found 1543 [M]$^+$. $C_{76}H_{57}BF_4O_4P_4Ir_2 \cdot CH_2Cl_2$ (1714.37): calcd. C 53.95, H 3.47; found C 53.65, H 3.61.

**Reaction of $[Ir_2H\{PPh_2(o\text{-}C_6H_4CO)\}\{\mu\text{-}PPh_2(o\text{-}C_6H_4CO)\}_3]BF_4$ (7) with HCl:** HCl gas was bubbled at room temperature through a methanol solution of **7** (30 mg, 0.018 mmol) for 30 min, upon which a small amount of precipitate was formed. The solvent was evaporated and the residue analyzed by NMR spectroscopy. According to the spectra, the solid contained mainly complex **1**.

**X-ray Structure Determination of 5 and 7:** Yellow prismatic single crystals of **5** and needles of **7** suitable for X-ray diffraction were successfully grown by slow diffusion of diethyl ether into dichloromethane or methanol solutions, respectively. Data collection was carried out at room temperature on a Bruker Smart CCD diffractometer, using graphite-monochromated Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å), operating at 50 kV and 20 mA. In both cases, data were collected over a hemisphere of the reciprocal space by combination of three exposure sets. Each exposure of 10 s covered 0.3° in $\omega$. The first 100 frames were recollected at the end of the data collection to monitor crystal decay after X-ray exposition; no appreciable drop in the intensities was observed. A summary of the fundamental crystal data for the crystals is given in Table 3. The structures were solved by direct methods and conventional Fourier techniques. The refinement was done by full-matrix least squares on $F^2$ for **5** and by blocked full-matrix least squares on $F^2$ for **7**.[30] Anisotropic parameters were used in the last cycles of refinement for all non-H atoms, with some exceptions. The $BF_4^-$ anions in both compounds were refined by three isotropic cycles and in subsequent cycles their thermal parameters were kept constant while their coordinates were refined with geometric restraints and a variable common B–F distance. For **7**, the carbon atoms of some phenyl rings were refined isotropically. After the last cycles of refinement, the Fourier difference of **5** showed some residual electronic density. This was assigned to one half solvent $CH_2Cl_2$. The carbon and chlorine atoms were treated like the $BF_4^-$ anions, i.e. three isotropic cycles and geometrical restraints. All hydrogen atoms were calculated at geometrical positions and refined as riding on their respective carbon atoms, except the hydride atoms (H1A, H1B) and the enolic hydrogen atoms (H2A, H2B) for **5**, which were found in a difference Fourier synthesis and their coordinates and thermal parameters fixed. For **7**, it was impossible to locate the hydride ions. These features led to $R1$ factors of 0.0585 (6212 reflections observed) and 0.0553 (8848 reflections observed) for **5** and **7**, respectively. The largest residual peaks in the final difference map (1.54 and 1.62 e Å$^{-3}$, respectively) were found in the vicinity of the fluorine atoms of the $BF_4^-$ groups in both compounds. CCDC-606708 (**5**) and -606709 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/datarequest/cif.

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[1] C. P. Casey, C. J. Czerwinski, K. A. Fusie, R. K. Hayashi, *J. Am. Chem. Soc.* **1997**, *119*, 3971–3978.

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

[3] a) M. Solà, T. Ziegler, *Organometallics* **1996**, *15*, 2611–2618; b) P. Cheliatsidou, D. F. S. White, D. J. Cole-Hamilton, *Dalton Trans.* **2004**, 3425–3427.

[4] a) C. M. Lukehart, *Acc. Chem. Res.* **1981**, *14*, 109–116; b) C. M. Lukehart, *Adv. Organomet. Chem.* **1986**, *25*, 45–71.

[5] C. M. Lukehart, G. P. Torrence, *Inorg. Chem.* **1979**, *18*, 3150–3155.

[6] D. Steinborn, *Dalton Trans.* **2005**, 2664–2671.

[7] a) D. Steinborn, M. Gerish, F. W. Heinemann, C. Bruhn, *Chem. Commun.* **1997**, 843–844; b) M. Gerish, C. Bruhn, A. Porzel, D. Steinborn, *Eur. J. Inorg. Chem.* **1998**, 1655–1659.

[8] M. A. Garralda, R. Hernández, L. Ibarlucea, E. Pinilla, M. R. Torres, *Organometallics* **2003**, *22*, 3600–3603.

[9] F. Acha, M. A. Garralda, L. Ibarlucea, E. Pinilla, M. R. Torres, *Inorg. Chem.* **2005**, *44*, 9084–9091.

[10] G. A. Lawrance, *Chem. Rev.* **1986**, *86*, 17–33.

[11] R. Schibli, R. Alberto, U. Abram, S. Abram, A. Egli, P. A. Schubiger, T. A. Kade, *Inorg. Chem.* **1998**, *37*, 3509–3516.

[12] a) B. Olgemöller, W. Beck, *Inorg. Chem.* **1983**, *22*, 997–998; b) W. Beck, K. Sünkel, *Chem. Rev.* **1988**, *88*, 1405–1421.

[13] W. J. Geary, *Coord. Chem. Rev.* **1971**, *7*, 81–122.

[14] M. Stradiotto, K. L. Fudjala, T. D. Tilley, *Chem. Commun.* **2001**, 1200–1201.

[15] T. G. Appleton, H. C. Clark, L. E. Manzer, *Coord. Chem. Rev.* **1973**, *10*, 335–422.

[16] a) D. Cuervo, J. Díez, M. P. Gamasa, J. Gimeno, *Organometallics* **2005**, *24*, 2224–2232; b) M. D. Curtis, N. A. Fatinos, *J. Organomet. Chem.* **1984**, *272*, 43–54.

[17] P. H. M. Budzelaar, *gNMR Software*, version 5.0, Adept Scientific plc, Letchworth, UK, **2004**.

[18] G. J. H. Buisman, L. A. van der Veen, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Organometallics* **1997**, *16*, 5681–5687.

[19] R. Shafiq, K. W. Kramarz, R. Eisenberg, *Inorg. Chim. Acta* **1993**, *213*, 111–119.

[20] B. D. Roswell, R. McDonald, M. Cowie, *Organometallics* **2004**, *23*, 3873–3883.

[21] J. M. O'Connor, R. Merwin, A. L. Rheingold, M. L. Adams, *Organometallics* **1995**, *14*, 2102–2105.

[22] C. Bianchini, E. Farnetti, M. Graziani, G. Nardin, A. Vacca, F. Zanobini, *J. Am. Chem. Soc.* **1990**, *112*, 9190–9197.

[23] a) C. J. Adams, M. I. Bruce, O. Kühl, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **1993**, *445*, C6–C9; b) C. J. Adams, M. I. Bruce, P. A. Duckworth, P. A. Humphrey, O. Kühl, E. R. T. Tiekink, W. R. Cullen, P. Braunstein, S. Coco, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **1994**, *467*, 251–281.

[24] C. M. Lukehart, L. J. Warfield, *Inorg. Chim. Acta* **1980**, *41*, 105–111.

[25] D. J. Liston, C. A. Reed, C. W. Eigenbrot, W. R. Scheidt, *Inorg. Chem.* **1987**, *26*, 2740–2741.

[26] D. Carmona, F. Viguri, F. J. Lahoz, L. A. Oro, *Inorg. Chem.* **2002**, *41*, 2385–2388.

[27] D. Carmona, L. A. Oro, M. P. Lamata, M. L. Jimeno, J. Elguero, A. Belguise, Ph. Lux, *Inorg. Chem.* **1994**, *33*, 2196–2203.

[28] D. Steinborn, M. Gerish, C. Bruhn, J. A. Davies, *Inorg. Chem.* **1999**, *38*, 680–683.

[29] R. M. Bullock, *Chem. Eur. J.* **2004**, *10*, 2366–2374.

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

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