

Oxidative Additions of Transition Metal–Hydrogen Bonds: Reactions of $\text{CpM}(\text{CO})_3\text{H}$ ($\text{M} = \text{Mo}, \text{W}$) with $[\text{tBuP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2]\text{M}'\text{Cl}$ ($\text{M}' = \text{Rh}, \text{Ir}$)[☆]

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Received January 16, 1996

Key Words: Oligophosphane complexes / Metal–Hydrogen bonds / Hydrogen transfer

Treatment of $(\text{PP}_2)\text{IrCl}$ [$\text{PP}_2 = \text{tBuP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2$] with an equimolar quantity of $\text{CpM}(\text{CO})_3\text{H}$ ($\text{M} = \text{Mo}, \text{W}$) or with HCl in THF resulted in smooth protonation of the d^8 substrate producing $[(\text{PP}_2)\text{Ir}(\text{H})\text{Cl}]\text{X}$ [$\text{X}^- = [\text{CpMo}(\text{CO})_3]^-$ (1), $[\text{CpW}(\text{CO})_3]^-$ (2), Cl^- (3)]. Combination of $(\text{PP}_2)\text{IrCl}$ and $\text{CpM}(\text{CO})_3\text{H}$ in a 2:1 stoichiometry gave $(\text{PP}_2)\text{Ir}(\text{H})\text{Cl}_2$ (7) together with $[(\text{PP}_2)\text{IrCO}][\text{Mo}(\text{CO})_3\text{Cp}]$ (8) or $[(\text{PP}_2)\text{IrCO}][\text{W}(\text{CO})_3\text{Cp}]$ (9). The rhodium analogues $(\text{PP}_2)\text{Rh}(\text{H})\text{Cl}_2$ (4), $[(\text{PP}_2)\text{RhCO}][\text{Mo}(\text{CO})_3\text{Cp}]$ (5), and $[(\text{PP}_2)\text{RhCO}][\text{W}(\text{CO})_3\text{Cp}]$ (6) were obtained similarly from $(\text{PP}_2)\text{RhCl}$ and $\text{CpM}(\text{CO})_3\text{H}$. Structural assignments for $[(\text{PP}_2)\text{Ir}(\text{H})\text{Cl}]^+$ and $(\text{PP}_2)\text{M}'(\text{H})\text{Cl}_2$ ($\text{M}' = \text{Rh}, \text{Ir}$) as diastereomers in which the hydrido ligand and the *t*Bu substituent on the central phosphorus atom are located on the same side or on

opposite sides of the PP_2 reference plane of the meridionally bound $\text{tBuP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2$ ligand are made on the basis of (i) correlations with known structures and reactivities of similar $[(\text{RP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PR}'_2)_2\text{M}'(\text{H})\text{Cl})]^+$ cations and (ii) an X-ray structure determination of 4. The crystal structure analysis of a $[(\text{PP}_2)\text{RhCO}]^+$ salt, closely related to 5/6 and 8/9, $[(\text{PP}_2)\text{Rh}(\text{CO})][\text{OCO}_2\text{H}]$ (10), demonstrates that in the solid state the four-coordinate $[(\text{PP}_2)\text{RhCO}]^+$ cation and its counterion exist as essentially charge-neutralized $\text{Rh}\cdots\text{O}$ -contacted ion pairs, two of which are linked by $\text{O}-\text{H}\cdots\text{O}$ bridges to centrosymmetric dimers. Ion pairing was also observed by IR spectroscopy for THF solutions of metalates 5/6 and 8/9.

Main group E–H fragments of bond polarities as disparate as C–H and Cl–H are well known for their tendency to oxidatively add to coordinatively unsaturated complexes of Rh^{I} , Ir^{I} , and Pt^0 . In contrast, analogous transformations of the transition metal–H bond are not well documented, the smooth formation of *cis*-(Ph_3P)₂ $\text{Pt}(\text{H})-\text{ReH}(\text{CO})_2\text{Cp}$ ^[1] and *cis*-(Ph_3P)₂ $\text{Pt}(\text{H})-\text{Mo}(\text{CO})_3\text{Cp}$ ^[2] from $(\text{C}_2\text{H}_4)\text{Pt}(\text{PPh}_3)_2$ and $\text{CpRe}(\text{CO})_2\text{H}_2$ or $\text{CpMo}(\text{CO})_3\text{H}$ representing notable exceptions. Similar reactions of several Vaska-type derivatives, *trans*- $\text{IrX}(\text{CO})(\text{PC}_6\text{H}_4\text{R}-4)_2$ ($\text{X} = \text{Cl}, \text{CH}_3$; $\text{R} = \text{H}, \text{CH}_3$), with $\text{CpRe}(\text{CO})_2\text{H}_2$ ^[1,3] or $\text{CpM}(\text{CO})_3\text{H}$ ($\text{M} = \text{Mo}, \text{W}$)^[4,5] did not lead to stable M–H addition products but instead afforded mononuclear^[1,3] or heterobinuclear^[4,5] derivatives resulting from secondary ligand exchange and P–C cleavage reactions. To circumvent such complicating dissociation/substitution equilibria of labile monodentate phosphanes in reactions between transition metal hydrides and coordinatively unsaturated d^8 complexes we decided to use four-coordinate Rh^{I} and Ir^{I} derivatives with flexible chelating tris(phosphane) ligands as 16e substrates. By doing so we anticipated to simultaneously achieve: (i) better control on stoichiometry and coordination number of the

resulting products by reducing the susceptibility of coordinated phosphane to become displaced, (ii) a more predictable stereochemistry of the complexes obtained by fixing the relative positions of the phosphanyl groups, and (iii) increased basicity (or nucleophilicity) at the metal center by permitting the Rh or Ir atom to adopt a defined coordination geometry maximizing combined inductive and chelation effects^[6,7]. In this article we therefore report on reactions of molybdenum and tungsten hydrides $\text{CpM}(\text{CO})_3\text{H}$ with chlororhodium(I) and -iridium(I) complexes of the tridentate chelating ligand $\text{tBuP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2$ ^[8,9], hereafter designated “ PP_2 ”.

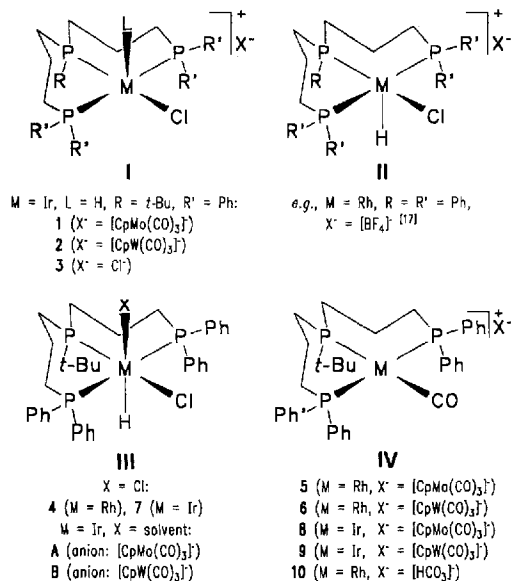
Results and Discussion

The metal-basic iridium(I) complex $(\text{PP}_2)\text{IrCl}$ underwent irreversible transformation into its conjugate acid, $[(\text{PP}_2)\text{Ir}(\text{H})\text{Cl}]^+$, when combined with equimolar $\text{CpMo}(\text{CO})_3\text{H}$ or $\text{CpW}(\text{CO})_3\text{H}$ in THF. The cream-colored precipitates so obtained showed conductance values in DMSO, $\Lambda = 83$ and $85 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$, consistent with their assignments as 1:1 electrolytes $[(\text{PP}_2)\text{Ir}(\text{H})\text{Cl}][\text{CpM}(\text{CO})_3]$; $\text{M} = \text{Mo}$ (1), W (2). A closely related salt-like compound $[(\text{PP}_2)\text{Ir}(\text{H})\text{Cl}]\text{Cl}$ (3) ($\Lambda = 84 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$ in MeCN) was isolated when HCl gas was bubbled through THF solu-

[◇] Part XL: A. Saare, L. Dahlenburg, *Z. Naturforsch. B: Chem. Sci.* **1995**, 50, 1009–1017.

tions of $(PP_2)IrCl$. All three complexes dissolved readily in DMSO and acetonitrile but proved to be only poorly soluble in acetone and THF. Addition of strong bases, e.g., pyridine or $LiN(SiMe_3)_2$, to solutions containing the $[(PP_2)Ir(H)Cl]^+$ cation resulted in its complete deprotonation to restore the starting $(PP_2)IrCl$ complex. The facile proton abstraction from $[(PP_2)Ir(H)Cl][CpW(CO)_3]$ (**2**) by pyridine was unexpected as earlier work had demonstrated that the hydride $CpW(CO)_3H$, which this work shows to behave as an acid toward the metal base $(PP_2)IrCl$ in THF, does not so toward the nitrogen base C_5H_5N in MeCN^[10,11].

In the 1H -NMR spectra, the IrH signals of complexes **1–3** displayed only little variation of their chemical shifts ($\delta = -19.6$ for **1** and **2** and -20.3 for **3**; all in $[D_6]DMSO$), the ^{31}P resonance patterns of their cations $1^+–3^+$ being virtually superimposable (see “Experimental”). Significantly, the three compounds all displayed small and approximately equal coupling constants $^2J(P,H)$ characteristic of hydrido ligands located *cis* to all three phosphorus atoms of a *mer*-bound PP_2 ligand in either of the two “top-bottom” diastereomers **I** and **II** ($M = Ir$, $L = H$, $R = tBu$, $R' = Ph$).



Formally related rhodium(III) cations, structurally assigned as diastereomers **I** ($M = Rh$, $R = R' = Ph$), have previously been obtained by treatment of $[PhP(CH_2CH_2CH_2PPh_2)_2]RhCl$ with the $[BF_4]^-$ or $[PF_6]^-$ salts of electrophiles L^+ such as $[R_3O]^+$, $[RC(O)]^+$, $[NO]^+$, or $[PhN_2]^+$ ^[6,12–17]. A common characteristic of these five-coordinate cations is that they do not associate Lewis-basic solvent molecules (EtOH, Me₂SO, MeCN, or SO₂) to form six-coordinate solvates $[[PhP(CH_2CH_2CH_2PPh_2)_2]Rh(L)(Cl)(\text{solv})]^+$, where the sixth ligand must fit into the highly crowded “bottom” site of **I**^[6,14,17]. Conversely, the seemingly analogous cationic fragments of $[[PhP(CH_2CH_2CH_2PPh_2)_2]Rh(H)Cl]X$ and $[[PhP(CH_2CH_2CH_2PCy_2)_2]Ir(H)Cl]X$ ($X^- = [BF_4]^-$, Cl^-) have a strong tendency to become six-coordinate

(either by solvation^[12,17,18] or addition of a halide anion^[12]), due to the small size of the metal-bound H ligand, which can fit into the “bottom” cavity of $[PhP(CH_2CH_2CH_2PPh_2)_2]RhCl$ or $[PhP(CH_2CH_2CH_2PCy_2)_2]IrCl$ forming diastereomeric structure **II** ($M = Rh$, Ir ; $R = Ph$, $R' = Ph$, Cy). Unlike these two species, the $[(PP_2)Ir(H)Cl]^+$ cation of **1** or **2** does not form detectable amounts of six-coordinate solvates $[(PP_2)Ir(H)Cl(\text{solv})]^+$ when the two salts are isolated from THF solution or crystallized from acetonitrile/ether mixtures. Another striking difference is the failure of $[(PP_2)Ir(H)Cl]^+$ to become coordinatively saturated by addition of its Cl^- counterion in complex **3**. Hence, the $[(PP_2)Ir(H)Cl]^+$ cation of **1–3** is attributed structure **I** ($M = Ir$, $L = H$, $R = tBu$, $R' = Ph$), in which the sterically non-demanding hydride blocks the relatively open metal site opposite from the *tert*-butyl substituent on the central phosphorus atom, thus preventing a more bulky additional ligand from completing the coordination sphere.

Reactions between $(PP_2)RhCl$ and $CpMo(CO)_3H$ or $CpW(CO)_3H$ in THF proceeded in a much more sluggish fashion than with $(PP_2)IrCl$ as the substrate complex to slowly precipitate yellow $(PP_2)Rh(H)Cl_2$ (**4**). From the supernatant mixture brown solids could be separated, which were originally formulated as $(PP_2)Rh-M(CO)_3Cp$ ($M = Mo$, W) on the basis of (i) the stoichiometry of a seemingly simple reaction “ $2(PP_2)RhCl + CpM(CO)_3H \rightarrow (PP_2)Rh-M(CO)_3Cp + (PP_2)Rh(H)Cl_2$ ”, (ii) the results of elemental analysis, and (iii) the appearance of their ^{31}P -NMR spectra (see below) and $\nu(CO)$ IR patterns [KBr]: $\tilde{\nu} = 1773$, 1892, 2008 cm^{-1} for $M = Mo$; 1771, 1887, 2008 cm^{-1} for $M = W$]. When, however, compared to the CO stretching frequencies of structurally defined heterobimetallics containing $CpM(CO)_3$ fragments directly bound to platinum metal atoms, e.g., $L(CNN)Pd-Mo(CO)_3Cp$ [$L = 4-MeC_5H_4N$, $CNN = 8\text{-methylquinolinyl-C,N}$; $\nu(CO)$: $\tilde{\nu} = 1827$, 1925, 2062 cm^{-1} in KBr]^[19], the $\nu(CO)$ absorptions at $\tilde{\nu} = 1770$ and 1890 cm^{-1} did not appear to be indicative of metal-bound $CpM(CO)_3$ groups but rather suggested the presence of carbonyl metalate anions existing in a non-cation-perturbed environment^[20]. Eventually, the alleged “ $(PP_2)Rh-M(CO)_3Cp$ ” complexes were identified as $[(PP_2)RhCO][M(CO)_3Cp]$, $M = Mo$ (**5**), W (**6**), containing the same monocarbonyl cation (formula **IV**) that had previously^[21] been encountered in the multi-component mixture of complexes obtained from exposing toluene solutions of the highly reactive dicyclohexylphosphido complex $(PP_2)RhPCy_2$ ^[22] to CO gas. Slow crystallization of the products so formed from their extremely air- and moisture-sensitive toluene/hexane solutions afforded, inter alia, single crystals of $[(PP_2)RhCO][HCO_3]$ (**10**), the cation of which displayed ^{31}P -NMR and $\nu(CO)$ -IR spectra closely matching those of the cation of **5** and **6**: $\delta(tBuP) = -5.3$ (-5.5), $\delta(PPh_2) = 9.9$ (9.2), $J(Rh, PtBu) = 109.8$ (113), $J(Rh, PPh_2) = 119.5$ (118), $J(P,P) = 49.5$ (49) Hz; $\nu(CO)$: $\tilde{\nu} = 2004$ (2008) cm^{-1} (data of **5** given in parentheses).

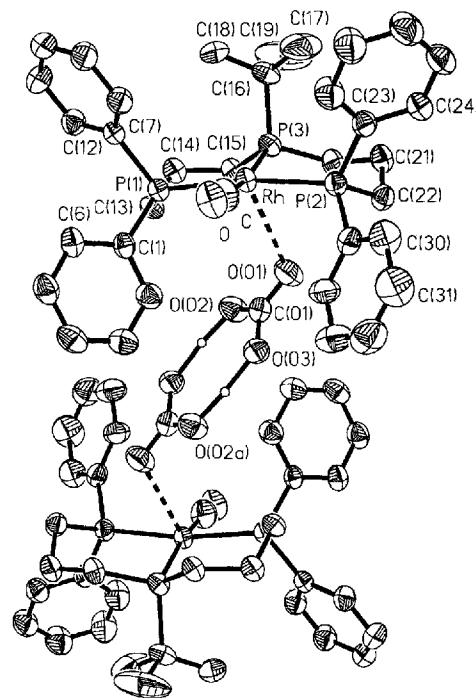
The characteristic structural features of the $[(PP_2)RhCO]^+$ cation, determined by an X-ray diffraction study

of hydrogen carbonate **10**, are (i) a *t*BuP–Rh bond [$d = 2.365(2)$ Å] lengthened with respect to the Ph₂P–Rh linkages [2.305(2) and 2.309(2) Å] by the *trans* bond-weakening influence of CO and (ii) a coordination geometry deviating substantially from planarity as evidenced from the interligand *trans* angles Ph₂P–Rh–PPh₂ [171.6(1)°] and *t*BuP–Rh–CO [168.8(2)°]. Slight tetrahedral distortion is a common structural characteristic of four-coordinate Rh^I complexes bearing tris(phosphane) ligands and has been described for a number of cationic and neutral species with general formula [RP(CH₂CH₂CH₂PR'₂)₂RhL]^{0/+} [8,23,24]. In the solid state, hydrogen carbonate **10** consists of essentially charge-neutralized Rh···O-contacted ion pairs, two of which are linked by O–H···O bonding to centrosymmetric dimers {[PP₂RhCO][OCO₂H]}₂ (Figure 1). There are few hydrogen carbonate complexes structurally characterized by X-ray diffraction. Relevant examples include *cis*-(2-H₂NC₅H₄N)₂Co(acac)O₂COH containing a bidentate hydrogen carbonate ligand^[25] and the unidentate hydrogen carbonates (dppe)Pd(OCO₂H)₂^[26], (Et₃P)₂(CH₃)PdOCO₂H^[27], and [Ph₃PNPPh₃][OC₅WOCO₂H]^[28], of which the latter two also form O–H···O-connected dimers. In all of the dimers the hydrogen bonds are quite tight resulting in O···O distances of 2.57 and 2.60 Å for the tungsten and palladium derivatives and 2.62 Å for Rh⁽⁺⁾···(–)OCO₂H ion pair **10**. Whereas the metal–oxygen bond lengths in the [(OC)₅WOCO₂H][–] anion (2.19 Å) and in the two palladium complexes (2.10 to 2.13 Å) adopt values typical of covalent metal–O bonding, there are only loose metal···anion contacts in **10** [$d(\text{Rh} \cdots \text{O}) = 3.18$ Å].

Weak Rh···O association is also observed for solutions of the two carbonyl metalate salts [(PP₂RhCO)[CpM(CO)₃], **5** and **6**. While the solid-state ν(CO)-IR spectra of these derivatives of the [(PP₂RhCO)]⁺ cation consist of only two [CpM(CO)₃][–] absorptions with band positions characteristic of these anions existing in a non-cation-perturbed C_{3v} structure (see above), the prevalent feature of the spectra in THF solution is the emergence of an additional low-frequency band at $\tilde{\nu} < 1750$ cm^{–1}, indicative of Cp(OC)₂–M–C≡O···M' interaction^[20]; ν(CO): **5**: $\tilde{\nu} = 1743, 1780, 1891, 2002$ cm^{–1}; **6**: 1741, 1778, 1888, 2001 cm^{–1}.

The iridium homologues of **4–6**, (PP₂)Ir(H)Cl₂ (**7**), [(PP₂)IrCO][Mo(CO)₃Cp] (**8**), and [(PP₂)IrCO][W(CO)₃Cp] (**9**) were formed when (PP₂)IrCl and the molybdenum or tungsten hydride were combined in 2:1 rather than 1:1 stoichiometry in THF at ambient conditions. Different from [(PP₂)Ir(H)Cl]Cl (**3**), dichlorohydrido-iridium complex **7** and its rhodium homologue **4** proved to be non-electrolytes in acetonitrile; i.e., unlike the [(PP₂)Ir(H)Cl]⁺ cation of **3**, the five-coordinate cationic fragments “[(PP₂)M(H)Cl]⁺” of the former two derivatives have a strong affinity for chloride ion, which becomes tightly bound in the uncrowded “top” site of **II** (M = Rh, Ir; R = *t*Bu, R' = Ph) to give **4** and **7** as covalent *apical*(H,Cl)-*anti* diastereomers **III** (M = Rh, Ir; X = Cl)^[29]. The *anti* configuration so deduced was confirmed by an X-ray structure determination of **4** (Figure 2). The Rh–Cl bond lengths [2.438(2) Å in *trans*-Cl–Rh–P vs. 2.540(3) Å in *trans*-Cl–Rh–H] as well

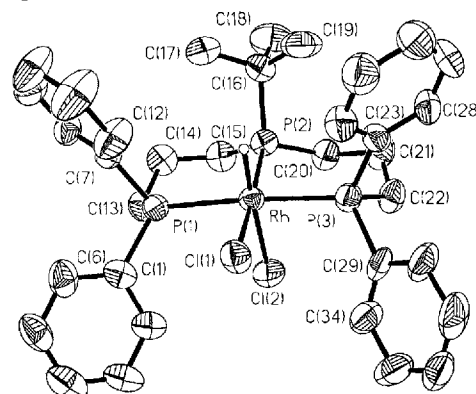
Figure 1. Molecular model of {[PP₂Rh(CO)][OCO₂H]}₂ (**10**)^[a]



[a] Selected bond lengths [Å] and angles [°]: Rh–P(1) 2.309(2), Rh–P(2) 2.305(2), Rh–P(3) 2.365(2), Rh–C 1.885(9), Rh···O(01) 3.18, C(01)–O(01) 1.25(1), C(01)–O(02) 1.28(1), C(01)–O(03) 1.31(1), O(03)···O(02a) 2.62; P(1)–Rh–P(2) 171.6(1), P(1)–Rh–P(3) 91.9(1), P(2)–Rh–P(3) 91.8(1), C–Rh–P(1) 88.8(2), C–Rh–P(2) 89.1(2), C–Rh–P(3) 168.8(2), O(01)–C(01)–O(02) 121.9(5), O(01)–C(01)–O(03) 119.4(5), O(02)–C(01)–O(03) 118.7(6).

as the Rh–P bond lengths [2.266(3) Å in *trans*-P–Rh–Cl vs. 2.332(3) and 2.325(3) Å in *trans*-P–Rh–P] exhibit the usual *trans*-compensating features originating from the different *trans* bond weakening capabilities of H, P, and Cl donor ligands.

Figure 2. Molecular model of (PP₂)Rh(H)Cl₂ (**4**)^[a]



[a] Selected bond lengths [Å] and angles [°]: Rh–P(1) 2.332(3), Rh–P(2) 2.266(3), Rh–P(3) 2.325(3), Rh–Cl(1) 2.438(2), Rh–Cl(2) 2.540(3), Rh–H 1.50(1); P(1)–Rh–P(2) 93.7(1), P(1)–Rh–P(3) 173.5(1), P(2)–Rh–P(3) 92.8(1), Cl(1)–Rh–Cl(2) 101.7(1), Cl(1)–Rh–P(1) 87.0(1), Cl(1)–Rh–P(2) 172.6(1), Cl(1)–Rh–P(3) 86.5(1), Cl(2)–Rh–P(1) 90.0(1), Cl(2)–Rh–P(2) 85.7(1), Cl(2)–Rh–P(3) 90.7(1).

Like **5** and **6**, carbonyl metalates **8** and **9** displayed ν(CO)-IR spectra congruent with the existence of their

anions either in a non-cation-perturbed symmetrical environment in the solid state [$\nu(\text{CO})$: **8** (Nujol): $\tilde{\nu} = 1771$, 1892, 1996 cm^{-1} ; **9** (CsI): $\tilde{\nu} = 1777$, 1890, 1996 cm^{-1}] or as cation-contacted species in THF solution [$\nu(\text{CO})$: **8**: $\tilde{\nu} = 1753$, 1784, 1896, 1998 cm^{-1} ; **9**: $\tilde{\nu} = 1750$, 1778, 1890, 1996 cm^{-1}]. In the more strongly coordinating solvent acetonitrile, the tungstate ion of **9** showed the two-band spectrum typical of the unperturbed anion [$\nu(\text{CO})$: $\tilde{\nu} = 1766$ (E) and 1886 (A_1) cm^{-1}] with an intensity of the E vibration corresponding to the collapse of the low-frequency $\text{W}(\text{CO})_2$ band and the $\text{WCO} \cdots \text{Ir}$ absorption of the cation-perturbed anion into that one vibration. This behaviour can be accounted for by solvent-separation of the $\text{Cp}(\text{OC})_2\text{-W}^{(-)}\text{-C}\equiv\text{O} \cdots \text{Ir}^{(+)}(\text{PP}_2)\text{CO}$ contact ion pair, i.e., formation of $[(\text{PP}_2)\text{Ir}(\text{CO})(\text{NCMe})]^+$ and symmetrically solvated $[\text{CpW}(\text{CO})_3]^-$; for similar solvent-separation of $\text{Cp}(\text{OC})_2\text{-M}^{(-)}\text{-C}\equiv\text{O} \cdots \text{Na}^{(+)}$ associated ion pairs by acetonitrile, see ref.^[20].

Formation of $[(\text{PP}_2)\text{IrCO}][\text{M}(\text{CO})_3\text{Cp}]$, **8** and **9**, also occurred when THF suspensions of $[(\text{PP}_2)\text{Ir}(\text{H})\text{Cl}][\text{CpM}(\text{CO})_3]$, **1** and **2**, were stirred for several days at ambient temperature. Under these conditions, carbonyl metalates **8** and **9** were accompanied by unseparable by-products **A** ($M = \text{Mo}$) and **B** ($M = \text{W}$), that were soluble only in polar solvents (e.g., THF, DMSO, and acetone) and displayed $\nu(\text{CO})$ -IR spectra characteristic of the presence of carbonyl metalate anions with unperturbed C_{3v} symmetry both in the solid state and in solution. In addition, these complexes could be assigned the following ^1H - and ^{31}P -NMR characteristics: **A** [**B**]: ^1H NMR ($[\text{D}_6]\text{DMSO}$): $\delta = -21.22$ [-21.23] [q, $J(\text{P,H}) = 14$ Hz, 1H, IrH]. ^{31}P NMR ($[\text{D}_6]\text{DMSO}$): $\delta = -20.8$ [-20.6] [d, $J(\text{P,P}) = 24$ Hz, 2P, PPh_2], -14.6 [-14.8] (t, 1P, $t\text{BuP}$). These data closely resemble those of *apical*(*H,Cl*)-*anti*-(PP_2) $\text{Ir}(\text{H})\text{Cl}_2$ (**7**) exhibiting, in $[\text{D}_6]\text{DMSO}$, $\delta(\text{IrH}) = -21.22$ [$J(\text{P,H}) = 13$ Hz], $\delta(\text{PPh}_2) = -20.1$ [$J(\text{P,P}) = 24$ Hz], and $\delta(t\text{BuP}) = -14.2$. Hence, complexes **A** and **B** are tentatively formulated as *apical*(*H,solv*)-*anti* diastereomeric salts $[(\text{PP}_2)\text{Ir}(\text{H})(\text{Cl})\text{-(solv)}][\text{CpM}(\text{CO})_3]$ (**III**, $M = \text{Ir}$, $X = \text{solvent molecule}$), arising from “top/bottom” isomerization (“**I** \rightarrow **II**”) and subsequent solvation (“**II** \rightarrow **III**”) of the $[(\text{PP}_2)\text{Ir}(\text{H})\text{Cl}]^+$ cation in **1** and **2**. **I/II** isomerization of five-coordinate $[(\text{PP}_2)\text{M}'(\text{H})\text{Cl}]^+$ cations ($M' = \text{Rh}, \text{Ir}$), followed by abstraction of chloride ion from unreacted $(\text{PP}_2)\text{M}'\text{Cl}$, would also account for the formation of the two *apical*(*H,Cl*)-*anti* diastereomeric dichlorohydrido complexes **4** and **7** observed both in the sluggish transformation of $(\text{PP}_2)\text{RhCl}$ by $\text{CpM}(\text{CO})_3\text{H}$ and in the smooth conversion of the molybdenum and tungsten hydrides by 2 equiv. of $(\text{PP}_2)\text{IrCl}$. The 14e fragments “ $[(\text{PP}_2)\text{M}']^+$ ” remaining after Cl^- transfer from $(\text{PP}_2)\text{M}'\text{Cl}$ to **I/II**-rearranged $[(\text{PP}_2)\text{M}'(\text{H})\text{Cl}]^+$ can be expected to be rapidly scavenged by CO giving the $[(\text{PP}_2)\text{M}'\text{CO}]^+$ cations of products **5/6** and **8/9**. It is worth noting that the metalate anions $[\text{CpM}(\text{CO})_3]^-$, representing the only conceivable CO sources in the reaction systems studied, are known to dissociate CO reversibly^[20]. Further support for the formation of cationic $[(\text{PP}_2)\text{M}'\text{CO}]^+$ by CO transfer from $[\text{CpM}(\text{CO})_3]^-$ to intermediately formed 14e

cores “ $[(\text{PP}_2)\text{M}']^+$ ” arises from the finding that metathetical displacement of chloride ion from $(\text{PP}_2)\text{RhCl}$ by a salt elimination reaction that employed $\text{Li}[\text{CpW}(\text{CO})_3]$ as the reactant also produced $[(\text{PP}_2)\text{RhCO}]^+$ salt **6** in appreciable yields.

Conclusions

This work has shown that the metal base $(\text{PP}_2)\text{IrCl}$ can interact with transition metal hydrides $\text{CpMo}(\text{CO})_3\text{H}$ [$pK_a(\text{MeCN}) = 13.9$] and $\text{CpW}(\text{CO})_3\text{H}$ [$pK_a(\text{MeCN}) = 16.1$]^[10,11] in the same way as with strong mineralic acids, e.g. HCl, yielding its conjugate acid $[(\text{PP}_2)\text{Ir}(\text{H})\text{Cl}]^+$ in reactions that may be considered to involve oxidative addition of a proton to iridium(I). Evidence is presented that the chloro hydrido cation, which is stable as a five-coordinate iridium(III) species, is initially generated as diastereomer **I** in which the hydride ligand occupies the more open “top” side of the metal coordination plane. In solution, the salts $[(\text{PP}_2)\text{Ir}(\text{H})\text{Cl}][\text{CpM}(\text{CO})_3]$ undergo slow degradation to $(\text{PP}_2)\text{Ir}(\text{H})\text{Cl}_2$ and $[(\text{PP}_2)\text{IrCO}][\text{M}(\text{CO})_3\text{Cp}]$, presumably via “top/bottom”-rearranged $[(\text{PP}_2)\text{Ir}(\text{H})\text{Cl}]^+$ cations **II**. Reactions between $(\text{PP}_2)\text{RhCl}$ and $\text{CpM}(\text{CO})_3\text{H}$ proceeded much slower than in the $(\text{PP}_2)\text{IrCl}/\text{CpM}(\text{CO})_3\text{H}$ system, $(\text{PP}_2)\text{Rh}(\text{H})\text{Cl}_2$ and $[(\text{PP}_2)\text{RhCO}][\text{M}(\text{CO})_3\text{Cp}]$ being the only products detected. There was no indication of reactions leading to heterobimetallics containing covalent Rh/Ir–Mo/W bonds which may be ascribed to the sterically demanding nature of the *tert*-butyl and phenyl substituents of the PP_2 ligand.

Clean protonation of metal-basic d^8 complexes by transition metal hydrides of intermediate thermodynamic acidity^[10,11] is, to the best of our knowledge, so far limited to the examples presented in this article. The reaction appears to depend critically on the electron richness of the substrate complex: While no reaction whatsoever occurred between *trans*- $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ and $\text{CpM}(\text{CO})_3\text{H}$ ($M = \text{Mo}, \text{W}$)^[5] proton transfer from the $M\text{--H}$ bond to the d^8 metal can be induced readily by substituting additional P donor groups for CO as has been demonstrated for the $(\text{PP}_2)\text{IrCl}/\text{CpM}(\text{CO})_3\text{H}$ systems studied before and will be confirmed further for several other $\text{IrX}(\text{PMe}_3)_4/\text{HML}_n$ pairs ($M = \text{Mn}, \text{Mo}, \text{W}, \text{Fe}, \text{Co}$)^[31] to be described elsewhere in near future.

Financial support by the *Fonds der Chemischen Industrie* (Frankfurt/Main) is gratefully acknowledged. We are also indebted to *De-gussa AG* (Hanau) for generous gifts of rhodium and iridium salts.

Experimental

All manipulations were performed under nitrogen using standard Schlenk techniques. Solvents employed were distilled from the appropriate drying agents prior to use. – IR: Mattson Polaris TM. – NMR: Jeol FT-JNM-GX 270 and Jeol FT-JNM-EX 270 [269.9 MHz (^1H), 67.7 MHz (^{13}C), and 109.4 MHz (^{31}P)], at $20 \pm 2^\circ\text{C}$ with TMS as internal or with H_3PO_4 as external standard (downfield positive).

{tert-Butylbis[3-(diphenylphosphanyl)propyl]phosphane}chlorohydrido-iridium(1+) Tricarbonyl(η^5 -cyclopentadienyl)molybdate-(1-) (**1**): A solution of 1.50 g (1.95 mmol) of $(\text{PP}_2)\text{IrCl}$ ^[9] and 0.50 g (2.03 mmol) of $\text{CpMo}(\text{CO})_3\text{H}$ in 30 ml of THF was stirred for

3 h at room temp. to cause the deposition of **1** as a cream-colored precipitate, which was recrystallized from acetonitrile/diethyl ether at -20° ; yield 1.15 g (58%). – IR (KBr): $\tilde{\nu}$ = 1765, 1890 cm^{-1} (CO), 2259 (IrH). – ^1H NMR ($[\text{D}_6]\text{DMSO}$): δ = -19.57 [q, $J(\text{P,H})$ = 12.4 Hz, 1 H, IrH], 0.42 [d, $J(\text{P,H})$ = 14.6 Hz, 9 H, $\text{C}(\text{CH}_3)_3$], 4.98 (s, 5 H, C_5H_5). – ^{13}C NMR ($[\text{D}_6]\text{DMSO}$): δ = 86.14 (s, C_5H_5), 235.24 (s, CO). – ^{31}P NMR ($[\text{D}_6]\text{DMSO}$): δ = -14.6 [t, $J(\text{P,P})$ = 25 Hz, 1 P, tBuP], -10.9 (d, 2 P, PPh_2). – $\text{C}_{42}\text{H}_{47}\text{ClIrMoO}_3\text{P}_3$ (1016.4): calcd. C 49.64, H 4.66; found C 49.47, H 4.82.

{tert-Butylbis[3-(diphenylphosphanyl)propyl]phosphane}chlorohydrido-iridium(I+)Tricarbonyl(η^5 -cyclopentadienyl)tungstate(1-) (**2**): A procedure analogous to that for **1** was employed, using 1.50 g (1.95 mmol) of $(\text{PP}_2)\text{IrCl}$ and 0.70 g (2.10 mmol) of $\text{CpW}(\text{CO})_3\text{H}$ in 30 ml of THF as starting materials; pale yellow microcrystals (from acetonitrile/diethyl ether); yield 1.17 g (54%). – IR (CsI): $\tilde{\nu}$ = 262 cm^{-1} (IrCl); (KBr): $\tilde{\nu}$ = 1761, 1885 cm^{-1} (CO), 2259 (IrH); (Nujol): $\tilde{\nu}$ = 1759, 1883 cm^{-1} (CO); (DMSO): $\tilde{\nu}$ = 1769, 1887 cm^{-1} (CO). – ^1H NMR ($[\text{D}_6]\text{DMSO}$): δ = -19.57 [q, $J(\text{P,H})$ = 13.3 Hz, 1 H, IrH], 0.43 [d, $J(\text{P,H})$ = 15.0 Hz, 9 H, $\text{C}(\text{CH}_3)_3$], 5.01 (s, 5 H, C_5H_5). – ^{13}C NMR ($[\text{D}_6]\text{DMSO}$): δ = 84.40 (s, C_5H_5), 225.76 [s with ^{183}W satellites, $J(\text{W,C})$ = 198 Hz, CO]. – ^{31}P NMR ($[\text{D}_6]\text{DMSO}$): δ = -14.4 [t, $J(\text{P,P})$ = 25 Hz, 1 P, tBuP], -10.7 (d, 2 P, PPh_2). – $\text{C}_{42}\text{H}_{47}\text{ClIrO}_3\text{P}_3\text{W}$ (1104.3): calcd. C 45.68, H 4.29; found C 45.74, H 4.43.

{tert-Butylbis[3-(diphenylphosphanyl)propyl]phosphane}chlorohydrido-iridium(I+)Chloride (**3**): A slow stream of HCl gas was bubbled through a solution of 0.77 g (1.00 mmol) of $(\text{PP}_2)\text{IrCl}$ in 100 ml of THF. The mixture lost its orange color immediately, compound **3** beginning to precipitate as a colorless solid. Separation of the product from the solution was completed by partial removal of the solvent, addition of petroleum ether, and cooling to -20°C ; yield 0.75 g (93%). – IR (CsI): $\tilde{\nu}$ = 272 cm^{-1} (IrCl); (KBr): $\tilde{\nu}$ = 2214 cm^{-1} (IrH). – ^1H NMR ($[\text{D}_6]\text{DMSO}$): δ = -20.32 [q, $J(\text{P,H})$ = 14.8 Hz, 1 H, IrH], 1.10 [d, $J(\text{P,H})$ = 13.8 Hz, 9 H, $\text{C}(\text{CH}_3)_3$]. – ^{31}P NMR ($[\text{D}_6]\text{DMSO}$): δ = -15.4 [t, $J(\text{P,P})$ = 23 Hz, 1 P, tBuP], -11.4 (d, 2 P, PPh_2). – $\text{C}_{34}\text{H}_{42}\text{Cl}_2\text{IrP}_3$ (806.7): calcd. C 50.62, H 5.25; found C 51.11, H 5.72.

{tert-Butylbis[3-(diphenylphosphanyl)propyl]phosphane}dichlorohydridorhodium(III) (**4**) and *{tert-Butylbis[3-(diphenylphosphanyl)propyl]phosphane}carbonylrhodium(I+)Tricarbonyl(η^5 -cyclopentadienyl)molybdate(1-)* (**5**): A solution of 0.70 g (1.03 mmol) of $(\text{PP}_2)\text{RhCl}^{[8]}$ in 30 ml of THF was treated with 0.36 g (1.46 mmol) of $\text{CpMo}(\text{CO})_3\text{H}$. After stirring for 5 d at ambient conditions, complex **4** having separated from the mixture as a yellow solid was filtered off. Dilution of the filtrate with petroleum ether caused the precipitation of **5** as brownish yellow microcrystals that were purified further by reprecipitation from THF/petroleum ether; yield 0.30 g (32%). On the basis of IR and NMR spectroscopic findings, product **4** corresponded in all respects with that described in ref. [22]. – **5**: IR (KBr): $\tilde{\nu}$ = 1773, 1892, 2008 cm^{-1} (CO); (THF): $\tilde{\nu}$ = 1743, 1780, 1891, 2002 cm^{-1} (CO). – ^1H NMR (C_6D_6): δ = 0.588 [d, $J(\text{P,H})$ = 15.0 Hz, 9 H, $\text{C}(\text{CH}_3)_3$], 5.49 (s, 5 H, C_5H_5). – ^{31}P NMR (C_6D_6): δ = -5.5 [dt, $J(\text{Rh,P})$ = 113, $J(\text{P,P})$ = 49 Hz, 1 P, tBuP], 9.2 [dd, $J(\text{Rh,P})$ = 118 Hz, 2 P, PPh_2]. – $\text{C}_{43}\text{H}_{46}\text{MoO}_4\text{P}_3\text{Rh}$ (918.6): calcd. C 56.22, H 5.05; found C 56.64, H 5.28.

{tert-Butylbis[3-(diphenylphosphanyl)propyl]phosphane}dichlorohydridorhodium(III) (**4**) and *{tert-Butylbis[3-(diphenylphosphanyl)propyl]phosphane}carbonylrhodium(I+)Tricarbonyl(η^5 -cyclopentadienyl)tungstate(1-)* (**6**): By analogy to the procedure outlined before from 0.85 g (1.25 mmol) of $(\text{PP}_2)\text{RhCl}$ and 0.48 g

(1.44 mmol) of $\text{CpW}(\text{CO})_3\text{H}$ in THF (14 d at room temp.). – **6**: Yield 0.30 g (24%). – IR (KBr): $\tilde{\nu}$ = 1771, 1887, 2008 cm^{-1} (CO); (THF): $\tilde{\nu}$ = 1741, 1778, 1888, 2001 cm^{-1} (CO). – ^{31}P NMR (C_6D_6): δ = -6.2 [dt, $J(\text{Rh,P})$ = 114, $J(\text{P,P})$ = 47 Hz, 1 P, tBuP], 9.1 [dd, $J(\text{Rh,P})$ = 118 Hz, 2 P, PPh_2]. – $\text{C}_{43}\text{H}_{46}\text{O}_4\text{P}_3\text{RhW}$ (1006.5): calcd. C 51.31, H 4.61; found C 51.87, H 4.48. – Complex **6** was prepared in similar yield by treating a THF solution of 1.02 mol $\text{Li}[\text{CpW}(\text{CO})_3]$ [freshly prepared from 0.34 g (1.02 mmol) of $\text{CpW}(\text{CO})_3\text{H}$ and 0.17 g (1.02 mol) of $\text{LiN}(\text{SiMe}_3)_2$] with 0.65 g (0.95 mmol) of $(\text{PP}_2)\text{RhCl}$ for 24 h at ambient conditions. Dilution of the mixture with petroleum ether caused the separation of a brownish oil which was decanted. Solidification of the oily product was achieved by vigorous stirring under petroleum ether. The solids were extracted into toluene, and pure **6** was isolated from the filtered extracts by slow addition of petroleum ether.

{tert-Butylbis[3-(diphenylphosphanyl)propyl]phosphane}dichlorohydrido-iridium(III) (**7**) and *{tert-Butylbis[3-(diphenylphosphanyl)propyl]phosphane}carbonyliridium(I+)Tricarbonyl(η^5 -cyclopentadienyl)molybdate(1-)* (**8**): Stirring a solution of 1.32 g (1.71 mmol) of $(\text{PP}_2)\text{IrCl}$ and 0.21 g (0.85 mmol) of $\text{CpMo}(\text{CO})_3\text{H}$ in 100 ml of THF for 3 d at ambient temp. afforded an off-white precipitate of **7** [0.62 g (45%)], which was separated by filtration. Dropwise addition of petroleum ether to the mother liquor gave **8** as an orange-brown solid; yield 0.50 g (29%). – **7**: IR (CsI): $\tilde{\nu}$ = 266, 284 cm^{-1} (IrCl); (KBr): $\tilde{\nu}$ = 2238 cm^{-1} (IrH). – ^1H NMR ($[\text{D}_6]\text{DMSO}$): δ = -21.22 [q, $J(\text{P,H})$ = 13.1 Hz, 1 H, IrH], 0.45 [d, $J(\text{P,H})$ = 15.0 Hz, 9 H, $\text{C}(\text{CH}_3)_3$]. – ^{31}P NMR ($[\text{D}_6]\text{DMSO}$): δ = -20.5 [d, $J(\text{P,P})$ = 25 Hz, 2 P, PPh_2], -14.8 (t, 1 P, tBuP); (C_6D_6): δ = -22.1 [d, $J(\text{P,P})$ = 24 Hz, 2 P, PPh_2], -15.9 (t, 1 P, tBuP). – $\text{C}_{34}\text{H}_{42}\text{Cl}_2\text{IrP}_3$ (806.7): calcd. C 50.62, H 5.25; found C 50.19, H 5.76. – **8**: IR (KBr): $\tilde{\nu}$ = 1767, 1892, 1996 cm^{-1} (CO); (Nujol): $\tilde{\nu}$ = 1771, 1892, 1996 cm^{-1} (CO); (THF): $\tilde{\nu}$ = 1753, 1784, 1896, 1998 cm^{-1} (CO). – ^1H NMR ($[\text{D}_6]\text{DMSO}$): δ = 0.85 [d, $J(\text{P,H})$ = 13.9 Hz, 9 H, $\text{C}(\text{CH}_3)_3$], 5.00 (s, 5 H, C_5H_5). – ^{31}P NMR ($[\text{D}_6]\text{DMSO}$): δ = -12.7 [t, $J(\text{P,P})$ = 37 Hz, 1 P, tBuP], -1.5 (d, 2 P, PPh_2); (C_6D_6): δ = -14.9 [t, $J(\text{P,P})$ = 38 Hz, 1 P, tBuP], -2.4 (d, 2 P, PPh_2). – $\text{C}_{43}\text{H}_{46}\text{IrMoO}_4\text{P}_3$ (1007.9): calcd. C 51.25, H 4.60; found C 51.82, H 5.08.

{tert-Butylbis[3-(diphenylphosphanyl)propyl]phosphane}dichlorohydrido-iridium(III) (**7**) and *{tert-Butylbis[3-(diphenylphosphanyl)propyl]phosphane}carbonyliridium(I+)Tricarbonyl(η^5 -cyclopentadienyl)tungstate(1-)* (**9**) were prepared as given before by treating 0.78 g (1.01 mmol) of $(\text{PP}_2)\text{IrCl}$ with 0.17 g (0.51 mmol) of $\text{CpW}(\text{CO})_3\text{H}$ in 100 ml of THF for 3 d at room temp. – **9**: Yield: 0.31 g (28%). – IR (CsI): $\tilde{\nu}$ = 1777, 1890, 1996 cm^{-1} (CO); (CH_3CN): $\tilde{\nu}$ = 1766, 1886, 1992 cm^{-1} (CO); (THF): $\tilde{\nu}$ = 1750, 1778, 1890, 1996 cm^{-1} (CO). – ^1H NMR ($[\text{D}_6]\text{DMSO}$): δ = 0.80 [d, $J(\text{P,H})$ = 14.0 Hz, 9 H, $\text{C}(\text{CH}_3)_3$], 5.09 (s, 5 H, C_5H_5). – ^{31}P NMR ($[\text{D}_6]\text{DMSO}$): δ = -12.6 [t, $J(\text{P,P})$ = 37 Hz, 1 P, tBuP], -1.2 (d, 2 P, PPh_2). – $\text{C}_{43}\text{H}_{46}\text{IrO}_4\text{P}_3\text{W}$ (1095.8): calcd. C 47.13, H 4.23; found C 46.71, H 4.37.

X-ray Structure Determinations: Single-crystals of $(\text{PP}_2)\text{Rh}(\text{H})\text{Cl}_2$ (**4**) (size $0.2 \times 0.2 \times 0.2 \text{ mm}^3$) were grown from toluene. The specimen of $[(\text{PP}_2)\text{RhCO}][\text{HCO}_3]$ (**10**) (crystal size $0.3 \times 0.2 \times 0.3 \text{ mm}^3$) was separated from an attempted preparation of $(\text{PP}_2)\text{Rh}(\text{CO})\text{PCy}_2$ involving exposure of $(\text{PP}_2)\text{RhPCy}_2$ in toluene/hexane solution to CO gas^[21], which furnished complex **10** as an addition compound containing toluene of crystallization, viz. $[(\text{PP}_2)\text{RhCO}][\text{HCO}_3] \cdot 2 \text{ C}_7\text{H}_8$. The measurements were performed at ambient temp. on a Syntex P21 diffractometer using graphite-monochromated Mo- K_α radiation (λ = 0.7107 Å): Orientation matrix and unit cell parameters from the setting angles of >15 centered medium-angle reflec-

tions ($11^\circ < 2\theta < 30^\circ$); collection of the diffraction intensities by the $\theta/2\theta$ scan technique with variable scan rates ($2.0^\circ \text{ min}^{-1}$ to $29.3^\circ \text{ min}^{-1}$); data uncorrected for absorption or extinction. The structures were solved by Patterson and difference Fourier methods employing the SHELXS-86^[32] and SHELX-76^[33] program systems with scattering factors from the sources given therein and subsequently refined by full-matrix least-squares procedures on F with allowance for anisotropic thermal motion of all non-hydrogen atoms except those of the toluene molecules of crystallization. These were detected in positions displaying heavy rotational disorder about the normals to their ring planes, which could be resolved for one of the rings by assigning the respective carbon atoms split occupancies of 0.5 each (common $U_{\text{iso}} = 0.099$) but could not be clarified for the ring atoms of the second molecule (common $U_{\text{iso}} = 0.154$). No attempts were made to locate the side-chain carbon atoms adopting s.o.f.'s of 0.083 and 0.166 in these models. According to some of the U_{ij} 's of the *t*Bu C atoms, rotational disorder about the C–P bonds of both structures was suggested for these substituents, too, but was ignored during refinement. Except for the toluene molecules of solvation, H atoms were included in the molecular models (Figures 1 and 2) assuming ideal geometry [$d(\text{C}–\text{H}) = 0.96 \text{ \AA}$] and using riding models with common isotropic behaviour (Rh \bar{H} of **4** located from final ΔF maps). – **4**: $\text{C}_{34}\text{H}_{42}\text{Cl}_2\text{P}_3\text{Rh}$ (717.45); orthorhombic, *Pbca*, $a = 14.783(2)$, $b = 18.897(3)$, $c = 24.061(3) \text{ \AA}$, $V = 6721.5 \text{ \AA}^3$, $Z = 8$, $d_{\text{calcd.}} = 1.418 \text{ g cm}^{-3}$, $\mu(\text{Mo}–K\alpha) = 0.83 \text{ mm}^{-1}$; $4.5^\circ \leq 2\theta \leq 50^\circ$, 6790 reflections ($0 \leq h \leq +18$, $0 \leq k \leq +22$, $0 \leq l \leq +29$) collected, 5964 independent; $R = 0.062$, $R_w = 0.063$ for 362 parameters and 2921 data with $|F_o| > 4\sigma(F_o)$, $w = [\sigma^2(F_o) + 0.00079 (F_o^2)]^{-1}$. **10** · 2 C_7H_8 : $\text{C}_{50}\text{H}_{60}\text{O}_4\text{P}_3\text{Rh}$ (918.85); triclinic, $P\bar{1}$, $a = 10.459(8)$, $b = 11.924(6)$, $c = 18.582(12) \text{ \AA}$, $\alpha = 92.91(4)$, $\beta = 99.50(6)$, $\gamma = 98.03(5)^\circ$, $V = 2264.5 \text{ \AA}^3$, $Z = 2$, $d_{\text{calcd.}} = 1.348 \text{ g cm}^{-3}$, $\mu(\text{Mo}–K\alpha) = 0.57 \text{ mm}^{-1}$; $4.5^\circ \leq 2\theta \leq 50^\circ$, 8746 reflections ($0 \leq h \leq +12$, $-14 \leq k \leq +14$, $-22 \leq l \leq +22$) collected, 8011 independent; $R = 0.067$, $R_w = 0.068$ for 470 parameters and 6002 data with $|F_o| > 3\sigma(F_o)$, $w = 1$. – Further details including tables of positional and thermal parameters are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the registration number CSD-59175.

* Dedicated to Professor Dr. Erwin Weiß on the occasion of his 70th birthday.

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