Synthesis and characterization of $(PPr^i_3)_2(CO)HRu(\mu\text{-}H)(\mu\text{-}OMe)Ir(cod)$: an unusual example of a heterometallic complex containing a mixed hydrido–alkoxide bridge

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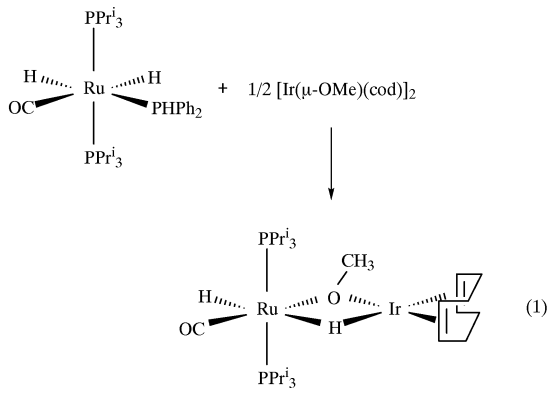
The complex $(PPr^i_3)_2(CO)HRu(\mu\text{-}H)(\mu\text{-}OMe)Ir(cod)$ (cod = cycloocta-1,5-diene) was obtained by treatment of $RuH_2(CO)(PHPh_2)(PPr^i_3)_2$ with $[Ir(\mu\text{-}OMe)(cod)]_2$. The structure of this heterodinuclear compound has been determined by X-ray diffraction analysis. The molecule is dinuclear and consists of a distorted square-planar coordination around iridium and a distorted octahedral coordination around ruthenium connected through a mixed hydrido–methoxy bridge. The Ru–Ir separation is 2.8635(5) Å.

It has been suggested that hydrido–alkoxide species are the key intermediates in the catalytic hydrogen transfer from alcohols to unsaturated organic substrates.[1,2] However, relatively few of such species have been isolated, since they appear to be thermodynamically and kinetically unstable with respect to either the elimination of alcohol or β-elimination from the alkoxide group.

Isolated complexes of this type are polynuclear compounds containing mixed hydrido–alkoxide bridges and include homodinuclear derivatives of Zr,[3] Nb,[4] Rh,[5] Ta[6] and W;[7] homotrinuclear compounds of Y,[8] Re[9] and Os;[10] homotetranuclear complexes of Mo[11] and W;[12] homopentanuclear derivatives of Ru[13] and homohexanuclear compounds of Ru.[14] In this work, we report the synthesis and characterization of the complex $(PPr^i_3)_2(CO)HRu(\mu\text{-}H)(\mu\text{-}OMe)Ir(cod)$ which, as far as we know, is the first isolated heterometallic compound containing a mixed hydrido–alkoxide bridge.

The complex is obtained as a yellow solid in 68% yield from the reaction of $RuH_2(CO)(PHPh_2)(PPr^i_3)_2$ with 0.5 equiv. of the dimer $[Ir(\mu\text{-}OMe)(cod)]_2$ [eqn. (1)].



(1)

A view of the molecular geometry is shown in Fig. 1. The hydrido ligands H(01) and H(02) were located in the difference Fourier maps and refined as isotropic atoms together with the remainder of non-hydrogen atoms of the structure giving Ru–H(0l) Ru–H(02) and Ir–H(02) distances of 1.57(6), 1.72(4) and 1.59(4) Å, respectively.

The molecule is dinuclear and consists of a distorted square-planar coordination around iridium and a distorted octahedron around ruthenium connected through a mixed hydrido–methoxy bridge [Ru–H(02)–Ir 120(3)°, Ru–O(2)–Ir 86.4(1)°]. The coordination sphere around the iridium atom is defined by the hydrido ligand H(02) situated *cis* to the methoxy group [O(2)–Ir–H(02) 78(2)°] and the two olefinic bonds [C(20)–C(21), C(24)–C(25)] of the diene. An ideal plane of the octahedral coordination around the ruthenium atom is formed and the carbonyl group and the terminal hydrido ligand are mutually *cis* disposed [H(01)–Ru–C(19) 91(2)°]; the hydrido ligand H(02) and the methoxy group are also *cis* disposed [O(2)–Ru–H(02) 73(2)°]. The triisopropylphosphine

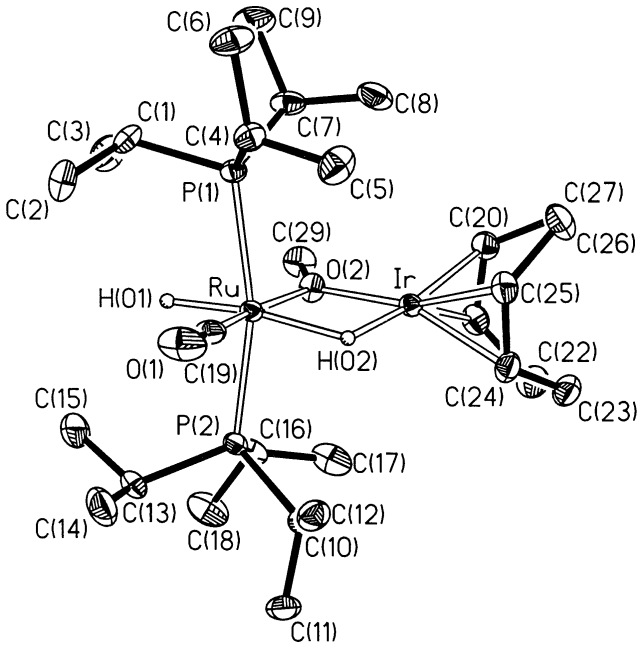


Fig. 1 Molecular diagram of $(PPr^i_3)_2(CO)HRu(\mu\text{-}H)(\mu\text{-}OMe)Ir(cod)$. Selected bond lengths (Å) and angles (°): Ru–Ir 2.8635(5), Ru–P(1) 2.408(1), Ru–P(2) 2.390(1), Ru–H(01) 1.57(6), Ru–C(19) 1.827(4), Ru–O(2) 2.134(3), Ru–H(02) 1.72(4), Ir–C(20) 2.149(4), Ir–C(21) 2.156(4), Ir–C(24) 2.127(4), Ir–C(25) 2.113(4), Ir–O(2) 2.046(3), Ir–H(02) 1.59(4), C(20)–C(21) 1.436(7), C(24)–C(25) 1.429(7); P(l)–Ru–P(2) 165.44(4), H(01)–Ru–C(19) 91(2), H(01)–Ru–H(02) 166(3), C(19)–Ru–O(2) 170.3(2), O(2)–Ru–H(01) 99(2), O(2)–Ru–H(02) 73(2), O(2)–Ir–H(02) 78(2), Ru–O(2)–Ir 86.4(1), Ru–H(02)–Ir 120(3).

ligands occupy *trans* axial positions [P(1)–Ru–P(2) 165.44(4)°].

Although, in general, M–H distances obtained from X-ray diffraction data are imprecise[15] the bond lengths in the Ru–H(02)–Ir sequence appears to reflect asymmetry in the hydrido bridge. In contrast to X-ray diffraction studies, *ab initio* calculations have been shown to provide useful accurate data for the hydrogen positions in both classical polyhydrides[16] and non-classical dihydrogen complexes.[17] So, in order to corroborate the asymmetrical coordination of H(02), we have performed a theoretical structure determination of $(PPr^i_3)_2$(CO)HRu(μ-H)(μ-OMe)Ir(cod) taking the complex $(PH_3)_2$(CO)HRu(μ-H)(μ-OMe)Ir$(C_2H_4)_2$ as a model (Fig. 2). In agreement with the X-ray data, the Ir–H_b distance (1.73 Å) is 0.21 Å shorter than the Ru–H_b (1.94 Å) bond length. These values are similar to those found in dinuclear ruthenium compounds, where a 'semi-bridging hydride ligand' has been proposed.[18]

The most remarkable feature of the structure of $(PPr^i_3)_2$(CO)HRu(μ-H)(μ-OMe)Ir(cod) is the Ru–Ir separation of 2.8635(5) Å. Although this distance is longer than that reported for the metal–metal bond bridged by two pyrazolyl ligands in the complex (η⁶-*p*-cymene)-RuCl(μ-pz)$_2$Ir$(CO)_2$ [2.6962(6) Å][19*a*] and that found in the trihydrido complex $(PPh_3)_3HRu(\mu\text{-}H)_2Ir$(cod) [2.6114(6) Å],[19*b*] it is shorter than the distances [2.879(1)–3.0306(6)(Å)] observed for the heterodinuclear compounds of the type $L'_{(2-n)}$(dppm)$_n$Ru(μ-H)(μ-L)Rh(cod)[18,20] and for $[(PPr^i_3)_2$-$(CO)_2$Ru(μ-H)(μ-pz)Rh(cod)]BF_4 [3.1323(3) Å],[21] where a hydrido bridged metal–metal bond (or metal–metal interaction) is proposed to exist.

According to the EAN rule, a single Ru–Ir bond could be present in $(PPr^i_3)_2$(CO)HRu(μ-H)(μ-OMe)Ir(cod). However, Green and coworkers[22] have proposed an alternative electron counting scheme for M–H–M systems, which does not require the presence of a single metal–metal bond. Furthermore, the counting scheme shows a direct relationship between the M–H–M and M–H–C bond angles. In agreement with the Green Scheme, EHT calculations on the complex $(\eta^5\text{-}C_5H_5)_2$Mo(μ-H)(μ-CO)Co$(CO)_3$ show that this species does not exhibit a single metal–metal bond,[23] in spite of the EAN rule predictions. Our recent EHT calculations on the model cation $[Ir_2H_2(PH_3)_4(\mu\text{-}H)_2(\mu\text{-}\kappa\text{-}O,\kappa\text{-}O\text{-}O_2CH)]^+$ also underline this trend. In this complex, the formal double bond between the iridium atoms is observed as a '*partial double bond*', where the bridge hydrido ligands play a substantial role.[24]

In order to establish whether the short Ru–Ir separation in $(PPr^i_3)_2$(CO)HRu(μ-H)(μ-OMe)Ir(cod) is due to some direct Ru–Ir interaction, we have performed a topological analysis of the electron density in the model compound $(PH_3)_2$(CO)-HRu(μ-H)(μ-OMe)Ir$(C_2H_4)_2$, on the basis of the Bader's atom-in molecules (AIM) theory.[25] Both the electron density and its Laplacian in the plane Ru(μ-H)(μ-OMe)Ir are shown in Fig. 3. The analysis of the Laplacian of the electron density in the region between both metals indicates the presence of a critical point of (3, +1) signature, characteristic of a ring point, which precludes the existence of some direct metal–metal interaction. On the other hand, it should be mentioned

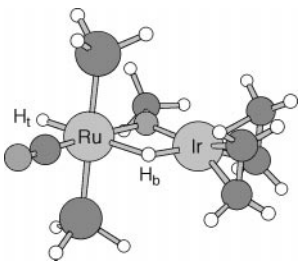


Fig. 2 Optimized structure of model complex $(PH_3)_2$(CO)HRu(μ-H)(μ-OMe)Ir$(C_2H_4)_2$ at the B3LYP-DFT level.

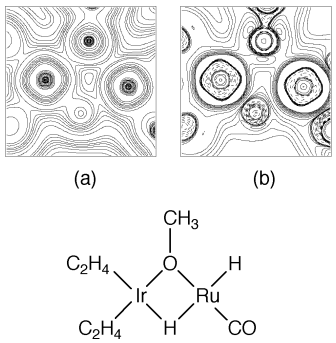


Fig. 3 Electron density map (a) and Laplacian (b) for model complex $(PH_3)_2$(CO)HRu(μ-H)(μ-OMe)Ir$(C_2H_4)_2$ in the plane Ir(μ-H)(μ-OMe)Ru.

that the eigenvalues perpendicular to the Ru–Ir vector are small, and the nature of the critical point between the metals could change with small changes in the electron density. A similar situation has been observed by Hall and coworkers for related systems.[26]

Both olefinic bond distances are essentially identical, 1.436(7) and 1.429(7) Å, while the Ir–C olefinic bond distances seem to be more sensitive to the asymmetry of the iridium coordination sphere, showing shorter values for the carbon atoms *trans* to the methoxy group [2.127(4) and 2.113(4) Å] than for those opposite to the hydrido ligand [2.149(4) and 2.156(4) Å]. Ru–P and Ru–CO distances are clearly in the range expected and require no further comment.

In agreement with the asymmetry of the iridium coordination sphere, the ^{1}H NMR spectrum of $(PPr^i_3)_2$(CO)HRu(μ-H)(μ-OMe)Ir(cod) in benzene-d_6 shows two resonances for the vinylic hydrogen atoms and two resonances for the aliphatic protons of the diene at δ 4.41, 3.82 and δ 2.27, 1.68, respectively, while the hydrido ligands display in the high field region two triplets at δ −7.12 [H(02)] and −7.78 [H(01)], with H–P coupling constants of 5.7 and 21.0 Hz, respectively. H–H coupling between H(01) and H(02) is not observed. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at δ 67.2. These spectroscopic data are in agreement with those previously reported for the complexes $(PPh_3)_2\{P(OMe)_3\}$HIr(μ-H)(μ-pz)Rh(diolefin) [diolefin = cod, tfb (tfb = tetrafluorobarrelene)][27] and $[(PPr^i_3)_2(CO)_2$Os(μ-H)(μ-pz)M(diolefin)]BF_4 (M = Rh, diolefin = cod, tfb; M = Ir, diolefin = cod).[28]

In conclusion, the reaction of the hydrido complex $RuH_2(CO)(PHPh_2)(PPr^i_3)_2$ with the dimer [Ir(μ-OMe)(cod)]$_2$ affords the unusual heterometallic derivative $(PPr^i_3)_2$-(CO)HRu(μ-H)(μ-OMe)Ir(cod) containing a mixed hydrido–alkoxide bridge. From a structural point of view, two features of this compound should be pointed out: (i) the asymmetrical coordination of the bridging hydrido ligand and (ii) the short Ru–Ir separation. Although the Ru–Ir distance [2.8635(5) Å] lies within the reported range where a hydrido bridged metal–metal bond is proposed to exist (2.61–3.13 Å), a topological analysis of the electron density in the model compound $(PH_3)_2$(CO)HRu(μ-H)(μ-OMe)Ir$(C_2H_4)_2$ suggests that, in this case, there is no direct metal–metal interaction, and therefore the Ru–H–Ir bond should be viewed as a typical three-center–two-electron bond.

Experimental

The reaction was carried out under an argon atmosphere by using Schlenk techniques. Solvents were dried and purified by known procedures and distilled under argon prior to use. The starting complexes $RuH_2(PHPh_2)(CO)(PPr^i_3)_2$[29] and [Ir(μ-OMe)(cod)]$_2$[30] were prepared by a published method. NMR spectra (^{1}H at 300 MHz and ^{31}P at 121.4 MHz) were recorded

at 293 K, and chemical shifts are expressed in ppm, upfield from $Si(CH_3)_4$ (^1H) and 85% H_3PO_4 (^{31}P). Coupling constants J and N [$N = J(HP) + J(HP')$ for ^1H] are given in Hz.

Computational details

The theoretical calculations were carried out on the model complex $(PH_3)_2(CO)HRu(\mu\text{-}H)(\mu\text{-}OMe)Ir(C_2H_4)_2$ by optimizing the structure at the MP2 and B3LYP-DFT levels with the Gaussian 94 program.[31] The symmetry of the complex was constrained to be C_s keeping the $Ru(\mu\text{-}H)(\mu\text{-}OCH_3)Ir$ plane as a symmetry plane. The basis sets used were, LANL2DZ basis and pseudopotentials for Ir and Ru, 6-31G* for the hydrido and phosphorous atoms and 6-31G for the rest of atoms.

Preparation of $(PPr^i_3)_2(CO)HRu(\mu\text{-}H)(\mu\text{-}OMe)Ir(cod)$

To a stirred suspension of $RuH_2(CO)(PHPh_2)(PPr^i_3)_2$ **1** (90 mg, 0.14 mmol) in 6 mL of methanol, was added $[Ir(\mu\text{-}OCH_3)(cod)]_2$ (47 mg, 0.07 mmol) and the mixture stirred for 1 h at reflux temperature with formation of a yellow solid. The solution was decanted, and the yellow solid was washed with methanol and dried *in vacuo*. Yield: 113 mg (68%). (Calc. for $C_{28}H_{59}IrO_2P_2Ru$: C, 42.95; H, 7.59. Found: C, 43.42; H, 7.16%). IR(Nujol, cm^{-1}): ν(Ru–H) 2015; ν(CO) 1891. ^1H NMR (300 MHz, C_6D_6): δ 4.41 (m, 2H, =C*H*, cod), 3.82 (m, 2H, =C*H*, cod), 3.36 (s, 3H, OCH_3), 2.27 (m, 4H, $-CH_2$, cod), 2.08 (m, 6H, $PCHCH_3$), 1.68 (m, 4H, $-CH_2$, cod), 1.44 (dvt, 18H, J_{HH} 6.9 Hz, N 12.9 Hz), 1.31 (dvt, 18H, J_{HH} 6.6 Hz, N 12.9 Hz), -7.12 (t, 1H, J_{HP} 5.7 Hz, Ru–μ-H), -7.78 (t, 1H, J_{HP} 21.0 Hz, Ru–H). $^{31}P\{^1H\}$NMR (121.4 MHz, C_6D_6): δ 67.2 (s).

X-Ray structure analysis of $(PPr^i_3)_2(CO)HRu(\mu\text{-}H)(\mu\text{-}OMe)$-Ir(cod)

Crystal data and data collection parameters. $C_{28}H_{59}IrO_2P_2Ru$; $M_w = 783.47$; yellow, prismatic crystal of dimensions $0.47 \times 0.40 \times 0.32$ mm; triclinic, space group $P\bar{1}$ (no. 2); $a = 8.6580(10)$, $b = 10.0400(10)$, $c = 19.371(2)$ Å; $\alpha = 92.860(10)$, $\beta = 93.180(10)$, $\gamma = 103.220(10)°$; $V = 1633.3(3)$ Å^3 (from 27 reflections $20 \leqslant 2\theta \leqslant 30°$); $Z = 2$, $D_c = 1.593$ g cm^{-3}; $\mu = 4.651$ mm^{-1}; four-circle Siemens-P4 diffractometer, Mo–Kα radiation (0.71073 Å), graphite-oriented monochromator; $T = 150$ K; $\omega - 2\theta$ scan method, max. $2\theta = 50°$; 6973 reflections measured, 5734 independent and 5718 used in refinement. All data were corrected for absorption.[32] The structure was solved by Patterson (SHELXTL-PLUS[33]) and conventional Fourier techniques, and refined by full-matrix least squares on F^2 (SHELXL93[34]). The hydrides were located and freely refined isotropically. The refinement converged to $R_1 = 0.0236$ [$F^2 > 2\sigma(F^2)$] and $wR_2 = 0.0809$ (all data) with weighting parameters $x = 0.0395$ and $y = 5.23$.

CCDC reference number 440/095. See http:/www.rsc.org/suppdata/nj/1999/403/ for crystallographic files in .cif format.

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