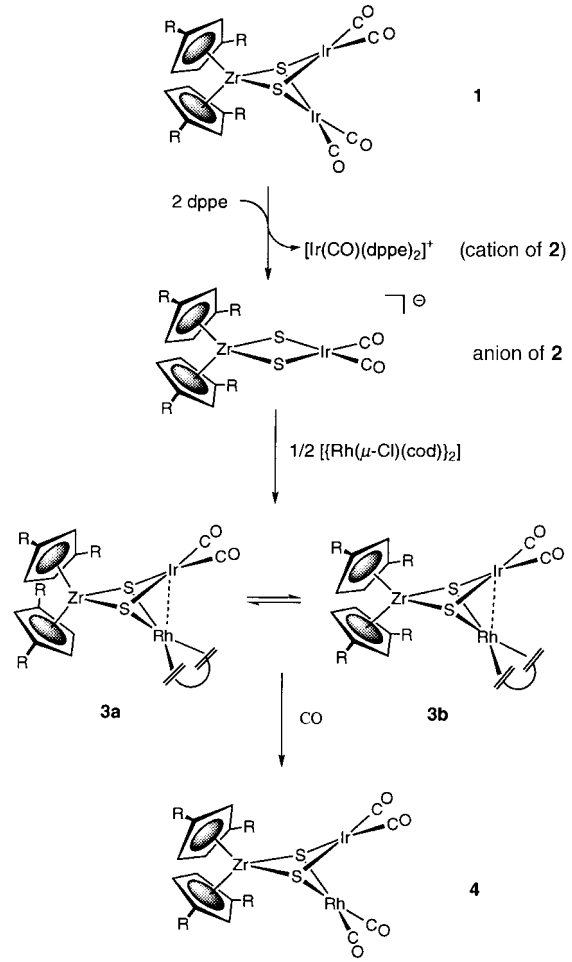
Controlled Synthesis of Early–Late Zr-Ir-Rh Heterotrimetallic Compounds by Metal Exchange Reactions**

Marc A. F. Hernandez-Gruel, Jesús J. Pérez-Torrente, Miguel A. Ciriano,* Fernando J. Lahoz, and Luis A. Oro*

Transition metal sulfide clusters have received wide attention because of their relevance to biological systems and industrial solid-surface catalysis.[1] However, the chemistry of metal–sulfur polynuclear compounds containing widely divergent transition metals—that is, early–late heterometallic complexes—is still poorly developed[2] despite their potential for new reactivity patterns in both catalytic[3] and stoichiometric reactions.[4] A goal is still to find ways to accommodate the differing electronic and coordination environments required by the metals in close proximity but still obtain stable compounds.[5] In this context, we recently reported that additive deprotonation reactions of $[Cp_2Ti(SH)_2]$ ($Cp = \eta^5$-C_5H_5) with methoxo-bridged dinuclear rhodium complexes make accessible the early–late heterobimetallic complexes $[CpTi(\mu_3\text{-}S)_3\{Rh(tfbb)\}_3]$ (tfbb = tetrafluorobenzobarralene) and $[\{CpTi\}_2(\mu_4\text{-}O)(\mu_3\text{-}S)_4\{Rh_4(CO)_4(PR_3)_2\}]$.[6] Here we report on the controlled synthesis of novel trinuclear early–late heterotrimetallic (ELHT) complexes driven by the zirconium metalloligand $[Cp^{tt}_2Zr(SH)_2]$, as well as some aspects of the reactivity of the early–late heterobimetallic (ELHB) precursors.

The new complex $[Cp^{tt}_2Zr(SH)_2]$ ($Cp^{tt} = \eta^5$-1,3-di-*tert*-butylcyclopentadienyl), prepared analogously to the related pentamethylcyclopentadienyl complex,[7] reacts with two molar equivalents of $[IrCl_2(CO)_2]^-$ in dichloromethane/methanol in the presence of triethylamine to give the trinuclear ELHB complex **1**, which was isolated in good yield (70%) as an apple-green solid.[8] Reaction of **1** with two molar equivalents of 1,2-bis(diphenylphosphanyl)ethane (dppe) in dichloromethane gave the ion-pair product **2** (Scheme 1), which was precipitated quantitatively with *n*-hexane as a highly air- and moisture-sensitive pale orange solid. A related precedent of this anion is the heterobimetallic complex $[Cp^*_2Zr(\mu\text{-}S)_2Rh(CO)_2]^-$ ($Cp^* = \eta^5$-C_5Me_5).[9]

Interestingly, the heterodinuclear anion $[Cp^{tt}_2Zr(\mu\text{-}S)_2Ir(CO)_2]^-$ behaves as a metalloligand towards d^8 metal centers and allows the synthesis of unprecedented Zr-Ir-Rh heterotrimetallic complexes. Reaction of **2** with 0.5 equivalents of



Scheme 1. Synthesis of heterotrimetallic complexes. R = *t*Bu.

$[\{Rh(\mu\text{-}Cl)(cod)\}_2]$ (cod = 1,5-cyclooctadiene) in dichloromethane gave **3** (Scheme 1), which was isolated as brown-orange microcrystals in 70% yield.

The molecular structure of **3** (Figure 1) shows a triangular ZrIrRh core capped on both sides by symmetrical μ_3-sulfido

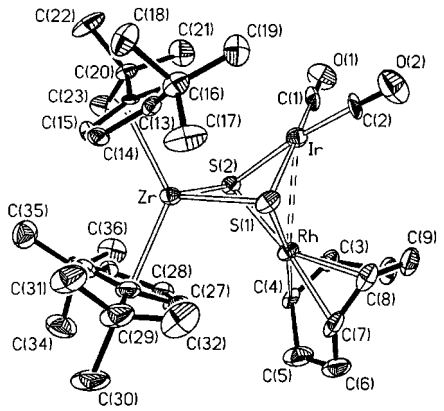


Figure 1. Molecular structure of **3**. Selected bond lengths [Å] and angles [°]: Zr–S(1) 2.506(3), Zr–S(2) 2.519(3), Zr–G(1) 2.290(9), Zr–G(2) 2.290(13), Ir–S(1) 2.417(3), Ir–S(2) 2.410(3), Ir–C(1) 1.838(13), Ir–C(2) 1.843(14), Rh–S(1) 2.411(3), Rh–S(2) 2.413(3), Rh–C(cod) 2.146–2.171(10); S(1)-Zr-S(2) 79.84(10), S(1)-Ir-S(2) 83.83(10), C(1)-Ir-C(2) 94.1(6), S(1)-Rh-S(2) 83.90(9), Zr-S(1)-Ir 87.41(9), Zr-S(2)-Ir 87.26(8), Zr-S(1)-Rh 84.02(9), Zr-S(2)-Rh 83.71(8), Ir-S(1)-Rh 71.50(8), Ir-S(2)-Rh 71.58 (8). G(1) and G(2) are the centroids of the cyclopentadienyl rings.

[*] Prof. Dr. L. A. Oro, Dr. M. A. Ciriano, Dr. M. A. F. Hernandez-Gruel, Dr. J. J. Pérez-Torrente, Dr. F. J. Lahoz
Departamento de Química Inorgánica
Instituto de Ciencia de Materiales de Aragón
Universidad de Zaragoza–CSIC
E-50009 Zaragoza (Spain)
Fax: (+34) 976761143
E-mail: oro@posta.unizar.es
mciriano@posta.unizar.es

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ligands.[10] If the metal–metal interactions are neglected, the d^8 rhodium and iridium centers exhibit square-planar coordination environments and the zirconium center has a distorted pseudo-tetrahedral geometry. Although no significant d^0-d^8 bonding interactions are present (Zr···Rh 3.2913(14), Zr···Ir 3.4018(15) Å), the Rh···Ir distance of 2.8205(10) Å lies in the expected range for a metal–metal bond. Slightly shorter Rh–Ir separations were found in $[Cp^*IrRhCl(CO)_2\{P(O\mathit{i}Pr)_3\}_2]$ (2.797(1) Å)[11] with an unsupported metal–metal bond and in the heterodinuclear complexes $[RhIr(CH_3)(CO)_3(\mu\text{-dppm})_2]^+$ (2.743(1) Å)[12] and $[RhIr(CO)_3(\mu\text{-dppm})_2]^+$ (2.7722(7) Å)[13] supported by two bis(diphenylphosphanyl)-methane (dppm) ligands. Longer metal–metal distances were found in the related cluster $[(Cp^*Ir)_2(\mu_3\text{-}S)_2Rh(cod)][RhCl_2(cod)]$ (2.906(1) and 2.913(9) Å).[14] The presence of a d^8-d^8 metal–metal interaction in **3** is also supported by the Rh-S-Ir angles (mean 71.54(6)°), which are smaller than the M-S-Zr angles (83.7–87.4°; M = Rh, Ir).

A remarkable feature of **3** is the fully staggered relative disposition of the Cp^{tt} ligands (Figure 2; G(1)-Zr-G(2) 129.8(4)°) in the Zr sandwich moiety, which results in C_s symmetry. This conformation differs greatly from the nearly

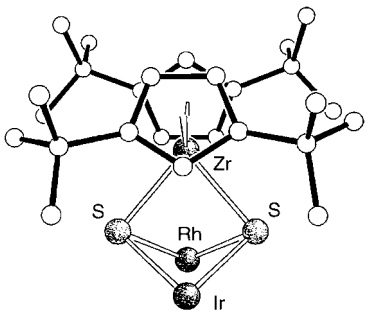

Figure 2. View of the Cp^{tt}_2Zr moiety of **3** perpendicular to the plane defined by Zr and the sulfido ligands. The staggered disposition of the Cp^{tt} ligands is evident.

eclipsed and straddle dispositions of $[Cp^{tt}_2TiCl_2]$[15a] and $[Cp^{tt}_2ZrI_2]$,[15b] respectively, probably as a consequence of the location of the bulky *tert*-butyl groups of the Cp^{tt} rings in the sterically least congested regions of the molecule. Complex **3** exists in $CDCl_3$ as two interconverting rotamers **3a** and **3b** (Scheme 1) in a 3:1 ratio, as shown by the negative cross-peaks in the phase-sensitive NOESY spectrum. Both C_s rotamers were unambiguously characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and two-dimensional NMR techniques, in particular, ^1H COSY, $^{13}C-^1H$ HETCOR, and NOESY. The major rotamer **3a** has a staggered arrangement of the *tert*-butyl groups, as is found in the solid state, whilst the spectroscopic data for the minor isomer **3b** suggest an eclipsed conformation. The Cp^{tt} ligand close to the Rh(cod) fragment in **3a** is easily distinguishable since the ring protons have unusual chemical shifts. Moreover, the observed NOE between two of the olefinic cod protons and the H4 and H5 protons of this Cp^{tt} ring corroborates their close proximity.

A restricted rotation of the Cp^{tt} ligand close to the more sterically demanding Rh(cod) fragment in **3** could account for the observation of the two rotamers in solution. However, neither a change in the ratio of the rotamers nor coalescence of the signals was observed in the ^1H NMR spectrum between 183 and 363 K in $[D_8]$toluene, although line-broadening effects are noticeable above room temperature. The activation parameters for the rotation of the Cp^{tt} ligand, obtained by the NMR spin-saturation transfer method in the range 308–276 K in $CDCl_3$, are $\Delta H^{\neq} = 19.2 \pm 1.5$ kcal mol^{-1} and $\Delta S^{\neq} = 6.7 \pm 2.6$ e.u. Energy barriers associated with the hindered rotation of η^5-cyclopentadienyl complexes are generally less than 13 kcal mol^{-1}.[16] Rotational barriers of 8.9 ± 0.5 kcal mol^{-1} were observed for the metallocene complexes $[Cp'_2TiCl_2]$[17a] and $[Cp'_2TiF_2]$[17b] (Cp′ = 1,3-bistrimethylsilylcyclopentadienyl). The larger value found for **3** ($\Delta G^{\neq}_{298} = 17.2$ kcal mol^{-1}) relative to the above-mentioned compounds is consistent with the larger steric hindrance of the metal fragments.

Carbonylation of **3** under atmospheric pressure in diethyl ether gives quantitatively the new ELHT complex **4** (Scheme 1), which was isolated as a green microcrystalline solid. Compound **4** can also be obtained in 70% yield in a one-pot synthesis starting from **1** by succesive addition of dppe and the anion $[RhCl_2(CO)_2]^-$.

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[8] Selected spectroscopic data for the new compounds: **1**: ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 6.74$ (t, $J(H,H) = 2.6$ Hz, 2H, H2), 6.24 (d, $J(H,H) = 2.6$ Hz, 4H, H4 and H5), 1.31 (s, 36H, Cp^{tt}); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 174.7$ (CO), 150.0 (C1 and C3), 127.5 (C2), 111.0 (C4 and C5), 35.1 (CMe_3), 32.1 (CH_3, Cp^{tt}); MS (FAB^+, CH_2Cl_2): *m*/*z* (%): 1006 (93) [M^+], 487 (100) [$M^+ - Cp^{tt}$]; IR (CH_2Cl_2): $\tilde{\nu}(CO) = 2056$ (s), 2027 (s), 1979 cm^{-1} (s). **2**: ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 7.70-6.80$ (m, 40H, dppe), 5.57 (d, $J(H,H) = 2.4$ Hz, 4H, H4 and H5, Cp^{tt}), 4.76 (t, $J(H,H) = 2.4$ Hz, 2H, H2, Cp^{tt}), 2.1 (m, 8H, CH_2, dppe), 1.21 (s, 36H, Cp^{tt}); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 25 °C): $\delta = 25.6$ (s); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 186.3$ (CO, $[Ir(CO)(dppe)_2]^+$), 179.6 (CO, $[Cp^{tt}_2Zr(\mu\text{-}S)_2\{Ir(CO)_2\}]^-$), 140.0 (C1 and C3, Cp^{tt}), 132.6 (m), 131.1 (br s), 128.6 (m, dppe), 108.0 (C_2), 99.8 (C4 and C5), 33.3 (CMe_3), 31.6 (CH_3, Cp^{tt}), 30.8 (m, CH_2, dppe); MS (FAB^+, $CDCl_3$): *m*/*z* (%): 989 (100) [$M^+ - CO$]; MS (FAB^-, $CDCl_3$): *m*/*z* (%): 757 (100) [M^-]; IR

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(CH_2Cl_2): $\tilde{\nu}$(CO) = 2004 (vs), 1947 (sh), 1931 cm^{-1} (vs). **3**: MS (FAB^+, CH_2Cl_2): *m*/*z* (%): 968 (100) [M^+], 791 (92) [$M^+ - Cp^{tt}$]; IR (CH_2Cl_2): $\tilde{\nu}$(CO) = 2023 (vs), 1954 cm^{-1} (vs); ^1H NMR (300 MHz, $CDCl_3$, 25 °C): rotamer **3a**: δ = 7.18 (d, *J*(H,H) = 2.4 Hz, 2H, H4 and H5), 6.60 (t, *J*(H,H) = 2.4 Hz, 1H, H2), 5.94 (d, *J*(H,H) = 2.4 Hz, 2H, H4 and H5), 5.83 (t, *J*(H,H) = 2.4 Hz, 1H, H2, Cp^{tt}), 4.42 and 4.19 (m, 2H each, =CH, cod), 2.7–2.4 (m, 2H), 1.9–2.2 (m, 4H), 1.8–1.6 (m, 2H, CH_2, cod), 1.32 and 1.26 (s, 18H each, Cp^{tt}); rotamer **3b**: δ = 6.69 and 6.38 (t, *J*(H,H) = 2.4 Hz, 1H each, H2), 6.03 and 5.90 (d, *J*(H,H) = 2.4 Hz, 2H each, H4 and H5, Cp^{tt}), 4.42 and 4.19 (m, 2H each, =CH, cod), 2.7–2.4 (m, 2H), 2.2–1.9 (m, 4H), 1.8–1.6 (m, 2H, CH_2 cod), 1.31 and 1.30 (s, 18H each, Cp^{tt}); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): rotamer **3a**: δ = 177.7 (CO), 150.0 and 142.2 (C1 and C3), 127.6 (C2), 119.7 (C4 and C5), 110.0 (C2), 105.5 (C4 and C5, Cp^{tt}), 84.0 and 80.6 (d, *J*(Rh-C) = 11.5 Hz, =CH, cod), 34.8 and 34.0 (CMe_3), 32.7 and 31.8 (CH_3, Cp^{tt}), 31.7 and 30.6 (CH_2, cod); rotamer **3b**: δ = 178.3 (CO), 147.2 and 147.1 (C1 and C3), 123.8 and 120.7 (C2), 109.5 and 108.8 (C4 and C5, Cp^{tt}), 85.9 and 80.6 (d, *J*(Rh,C) = 11.5 Hz, =CH, cod), 34.5 and 34.4 (CMe_3), 32.3 and 32.2 (CH_3, Cp^{tt}), 31.6 and 30.2 (CH_2, cod). **4**: ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 6.72 and 6.62 (t, *J*(H,H) = 2.5 Hz, 1H each, H2), 6.16 and 6.11 (d, *J*(H,H) = 2.5 Hz, 2H each, H4 and H5), 1.31 and 1.30 (s, 18H each, Cp^{tt}); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): δ = 184.9 (d, *J*(Rh,C) = 74 Hz, CO), 175.4 (CO), 149.4 and 149.1 (C1 and C3), 126.2 and 122.5 (C2), 110.1 and 110.0 (C4 and C5), 34.9 and 34.8 (CMe_3), 32.2 (CH_3, Cp^{tt}); MS (FAB^+, CH_2Cl_2): *m*/*z* (%): 916 (46) [M^+], 860 (100) [$M^+ - 2CO$], 739 (49) [$M^+ - Cp^{tt}$]; IR (CH_2Cl_2): $\tilde{\nu}$(CO) = 2062 (s), 2031 (s), 1996 (m), 1971 cm^{-1} (m).

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[10] Crystal data for **3**: $C_{36}H_{54}IrO_2RhS_2Zr$, M_r = 969.24, monoclinic, space group $P2_1/c$; a = 11.9123(9), b = 21.5742(17), c = 15.0796(12) Å, β = 105.526(2)°, V = 3734.0(5) $Å^3$, Z = 4, ρ_{calcd} = 1.724 $g\,cm^{-3}$, μ = 4.407 mm^{-1}. Crystal dimensions 0.12 × 0.16 × 0.18 mm. Bruker SMART CCD diffractometer, T = 153(1) K, graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073). A complete hemisphere of data was scanned on ω (0.30° per frame) with a run time of 20 s at the detector resolution of 512 × 512 pixel. Reflections were extracted by using the SAINT program, and Lorentzian, polarization, and absorption corrections were applied. Of 9398 reflections measured, 4506 were unique (R_{int} = 0.0657). The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least squares on F^2 (SHELXL-97). Anisotropic displacement parameters were used for all non-hydrogen atoms. Hydrogen atoms were included in calculated positions. 403 parameters, 18 restraints; R = 0.0509 (3512 reflections, $F \le 4\sigma F_o$), $R_w(F^2)$ = 0.1007 (all reflections), and S = 1.076. Max. residual electron density 1.05 $e\,Å^{-3}$ close to the Ir atom. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-116623. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Photomodulation of the Conformation of Cyclic Peptides with Azobenzene Moieties in the Peptide Backbone**

Raymond Behrendt, Christian Renner, Michaela Schenk, Fengqi Wang, Josef Wachtveitl, Dieter Oesterhelt, and Luis Moroder*

For photomodulation of conformational, physico-chemical, and biological properties of peptides, proteins, and phospholipids large use has been made of the *cis*/*trans* isomerization of azobenzene moieties grafted to specific sites of such biomaterials or related model systems.[1, 2] Since the light-induced isomerization of azobenzene is accompanied by significant changes in geometry and polarity of the chromophore,[3] this proved to be well suited for induction of local topochemical changes in conformationally more restricted small systems.[4–10] Low-mass cyclic peptides are rigid structures that are extensively exploited for the design of libraries of conformers of defined bioactivities.[11, 12] Thus, incorporation of the azobenzene moiety into the peptide backbone of such cyclic peptides is expected to represent an ideal system to probe the efficiency of this "light-switch" for induction of conformational transitions. With 4-(4-aminophenylazo)benzoyl (APB) as amino acid residue in the peptide backbone we succeeded in the present study to construct a very rigid, conformationally constrained cyclic peptide in the *trans* configuration which upon irradiation, relaxes into a largely free conformational space.

The distance between the two *para*-carbon atoms of the azobenzene unit in the *trans* configuration is 9 Å and in the *cis* configuration 5 Å. To transfer optimally these changes in geometry to the peptide backbone, H-APB-OH was synthesized according to known methods[13] and fully characterized in its photochemical properties.[14, 15] It was then incorporated into an octapeptide related to the active site of thioredoxine reductase (Scheme 1). Owing to the low nucleophilicity of the *para*-amino group of H-APB-OH, its protection in acylating the resin-bound peptide was not required, but difficulties were encountered in the subsequent acylation of this group. These were overcome by silylation and using the acid fluoride method for the peptide-chain extension step. Mild acidic cleavage from the resin produced the linear side chain protected pseudo-nonapeptide **1**, which was then cyclized by the PyBOP/HOBt/DIEA procedure. Final acidic deprotection generated the target compound **2** cyclo(Ala-Cys(S*t*Bu)-Ala-Thr-Cys(S*t*Bu)-Asp-Gly-Phe-APB).

Peptides **1** and **2** were characterized spectroscopically (Table 1). Compared to H-APB-OH [λ_{max} = 420 nm ($\pi - \pi^*$)

[*] Prof. Dr. L. Moroder, Dipl.-Chem. R. Behrendt, Dr. C. Renner, Dr. M. Schenk, Dr. F. Wang, Prof. Dr. D. Oesterhelt
Max-Planck-Institut für Biochemie
Am Klopferspitz 18A, D-82152 Martinsried (Germany)
Fax: (+49) 89-8578-2847
E-mail: moroder@biochem.mpg.de
Dr. J. Wachtveitl
Institut für Medizinische Optik der Universität
Oettingenstrasse 67, D-80538 München (Germany)

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