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Metal Ion Cooperativity in a Chloro-Bridged Zinc–Rhodium Heterobinuclear Metal Complex

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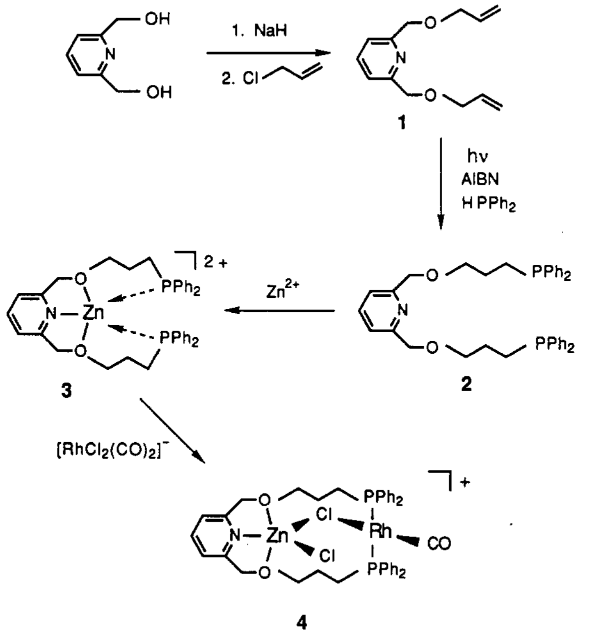
*Summary: A new heterobinucleating ligand, 2,6-bis[(3-(diphenylphosphino)propoxy)methyl]pyridine (**2**), is used to generate a Zn–Rh mixed-metal complex, {2[ZnCl(μ-Cl)Rh(CO)]}(CF_3SO_3), containing a Zn(II) Lewis acid ion in close proximity to a Rh(I) catalytic site. The metal ions are linked by a chloride bridge, resulting in an increased ν_{CO} value compared to that of mononuclear Rh(I) complexes in a similar coordination environment. The complex is an active hydroformylation catalyst, displaying no induction period for initiation of the reaction as is characteristic of mononuclear Rh species.*

Bimetallic catalysts containing a redox-active transition metal in close proximity to a Lewis acid site are of interest to study the effect of metal ion cooperativity on molecular activation.[1] Such systems have been suggested for the bifunctional activation of CO and, ultimately, the catalysis of C_1 transformations.[2] Some recent approaches taken to synthesize discrete metal complexes of this type have used heterobinucleating ligands possessing both hard and soft donor sites, usually phosphorus donors at the soft site and nitrogen and/or oxygen donors at the hard site.[3] Stepwise reaction of metal salts or organometallic precursors with these ligands has resulted in the assembly of mixed-metal complexes in which the metal centers are sufficiently close to each other to interact with a potentially bridging substrate molecule offering promise of binuclear cooperativity. Our efforts in this area have resulted in the synthesis of the new heterobinucleating ligand 2,6-bis[(3-(diphenylphosphino)propoxy)methyl]pyridine (2) and its zinc–rhodium complex 4. Attempts to synthesize mixed-metal complexes containing Lewis acids other than Zn, such as Mg(II), Al(III) and Gd(III), gave evidence for the formation of complexes with 2, but these intermediates did not incorporate Rh to yield isolable heterobinuclear species. We wish to report here the synthesis and X-ray structure of 4 and evidence for a cooperative interaction between the Zn(II) and Rh(I) ions via a chloride bridge.

Scheme I



The aza oxa phosphine 2 was prepared in 79% overall yield in the two-step reaction sequence shown in Scheme I. The deprotonation product of 2,6-pyridinedimethanol was alkylated with allyl chloride to form the bis(allyl ether) 1 in 87% yield.[4] Irradiation of a benzene solution of 1, in the presence of AIBN and a 30% excess of diphenylphosphine, gave 2 as a white solid in 91% yield.[5] Reaction of 2 with a slight excess of $Zn(O_3SCF_3)_2$,[6] as a suspension in

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(4) Compound 1: A stirred solution of NaH (1.49 g, 62.2 mmol) and 2,6-pyridinedimethanol (4.00 g, 28.7 mmol) in 60 mL of 1,2-dimethoxyethane was allowed to react under N_2 until H_2 evolution ceased (ca. 2 h). After the solution was concentrated to a volume of 20 mL under reduced pressure, 20 mL of allyl chloride (0.25 mol) was added. The reaction mixture was then refluxed for 48 h under N_2, the solvent removed under reduced pressure, and the residue extracted with CH_2Cl_2. The CH_2Cl_2 extract was washed with H_2O and dried over anhydrous K_2CO_3 and the CH_2Cl_2 removed under reduced pressure. Vacuum distillation of the resulting yellow oil gave 1 at 110 °C (1 mmHg) as a clear, colorless liquid in 87% yield. ^1H NMR ($CDCl_3$, TMS): δ 7.68 (t, 1H, 4-py), 7.35 (d, 2H, 3,5-py), 5.94 (m, 2H, CH=), 5.27 (dd, 4H, =CH_2), 4.62 (s, 4H, py–CH_2–O), 4.10 (d, 4H, OCH_2C=). $^{13}C\{^1H\}$ NMR ($CDCl_3$, TMS): δ 157.6 (2,6-py), 136.7 (4-py), 134.1 (CH=), 119.4 (3,5-py), 116.7 (=CH_2), 72.6 (py–CH_2–O), 71.4 (OCH_2C=).

(5) Compound 2: A solution of 1 (5.48 g, 24.7 mmol), diphenylphosphine (11 mL, 63 mmol), and AIBN (50 mg) in 10 mL of dry benzene was irradiated under N_2 for 72 h in a Rayonet Model RPR-100 photochemical reactor. Additional AIBN (50 mg in 10 mL of benzene) was added each day during the course of the irradiation. After removal of the benzene under reduced pressure, excess diphenylphosphine, AIBN, and 1 were removed by heating in a short-path-length distillation apparatus at 200 °C in vacuo for 5 h. The resulting yellow oil was eluted on a 4 × 7 cm column of neutral alumina (activity I) with 200 mL of benzene. Removal of the benzene under reduced pressure gave a clear, colorless oil which, when stirred in 100 mL of pentane, gave 2 as a white solid in 91% yield after isolation by filtration and drying in vacuo: mp 41–43 °C. ^1H NMR ($CDCl_3$, TMS): δ 7.65 (t, 1H, 4-py), 7.35 (m, 22H, 3,5-py, Ph), 4.57 (s, 4H, py–CH_2O), 3.62 (t, 4H, OCH_2CH_2), 2.11 (m, 4H, CH_2PPh_2), 1.75 (m, 4H, $CH_2CH_2CH_2$). $^{31}P\{^1H\}$ NMR (CH_2Cl_2, external H_3PO_4): δ −15.9.

(6) $Zn(O_3SCF_3)_2$ was prepared by modification of a published procedure.[24] Zinc oxide was treated with HO_3SCF_3 in MeOH. The resulting solution was refluxed for 2 h, the solvent removed under reduced pressure, and the white solid washed with CH_2Cl_2 and dried in vacuo at 125 °C for 2 h.

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dichloromethane, resulted in dissolution of the Zn salt to give [**2**(Zn)](CF_3SO_3)$_2$ (**3**) as a white solid in 92% yield.[7] ^{1}H NMR confirmed the placement of the Zn(II) ion in the "ONO" donor site, as indicated by the downfield shift of the ether methylene and pyridyl protons. The phosphine groups are weakly interacting with the Zn(II) center, as is indicated by the slight downfield shift from −15.9 to −9.5 ppm and broadening of the phosphorus resonances.

The heterobinuclear complex {**2**[ZnCl(μ-Cl)Rh(CO)]}(CF_3SO_3) (**4**) was prepared as a bright yellow solid in 60% yield by the slow addition of an equimolar quantity of [Bu_4N][$RhCl_2(CO)_2$][8] to **3** in dichloromethane.[9] Crystals suitable for X-ray diffraction[10] were grown by vapor diffusion of benzene into a nitromethane solution of **4**. The structure of the cationic part of **4** and selected bond lengths and angles are given in Figure 1. The square-planar Rh(I) ion is joined to a distorted-trigonal-bipyramidal Zn(II) ion by a chloride bridge with the entire assembly contained within the cavity of the ligand. As expected, the Zn(II) and Rh(I) ions are bound in the hard "ONO" and soft "PP" ligand sites, respectively. All of the Rh–P,[11,12] Zn–N,[13,14] Zn–O,[15,16] and Zn–Cl[15,17] bond lengths and angles are typical of those observed in similar mononuclear metal complexes, indicating that the ligand framework is flexible enough to accommodate regular coordination geometries in both chelating sites. However, an interesting feature of the structure results from the influence of the electropositive Zn(II) ion on the Rh center through the chloride bridge. Since the electron-donor strength of the bridged chloride to Rh is reduced by the Zn(II) ion, the Rh(1)–Cl(1) distance of 2.399 (4) Å is slightly elongated compared to those in $RhCl(CO)(PMePh_2)_2$ [2.362 (1) Å][12] and $RhCl(CO)(PPh_3)_2$ [2.371 (2) Å].[11] The resulting decreased electron density on the Rh center is reflected in the bond lengths of the Rh(1)–C(14) [1.84 (2) Å] and C(14)–O(3) [1.11 (2) Å] bonds. These values are at the high and low ends, respectively, of the range typically observed for mononuclear Rh complexes such as $RhCl(CO)(PMePh_2)_2$ [Rh–C, 1.795 (0) Å; C–O, 1.142 (1) Å][12] and $RhCl(CO)(PPh_3)_2$ [Rh–C, 1.810 (7) Å; C–O, 1.144 (8) Å].[11] In agreement with these structural features, the ν_{CO} value of 1995 cm^{-1} found in CH_2Cl_2 in the infrared spectrum is higher than that observed in mononuclear $RhCl(CO)(PR_3)_2$ species [$PEtPh_2$, 1968.5 cm^{-1}; $PMePh_2$, 1974 cm^{-1}],[18] in which the Rh is in a similar coordination environment. The decreased electron density on Rh in **4**, compared to the $RhCl(CO)(PR_3)_2$ species, results in a decreased back-bonding from Rh to the π^* orbitals of CO and a higher value of ν_{CO}. A similar asymmetry of the chloride bridge and increased CO infrared stretching frequency was observed in a homobinuclear dirhodium "A-frame" complex.[19] Also, NMR data in methylene chloride indicate that the binuclear complex maintains its structural integrity in solution. In the ^{31}P NMR spectrum, a doublet at +26.4 ppm with a J_{Rh-P} value of 119 Hz confirms the placement of Rh between mutually trans phosphorus atoms. Also, the ^{1}H NMR spectrum of

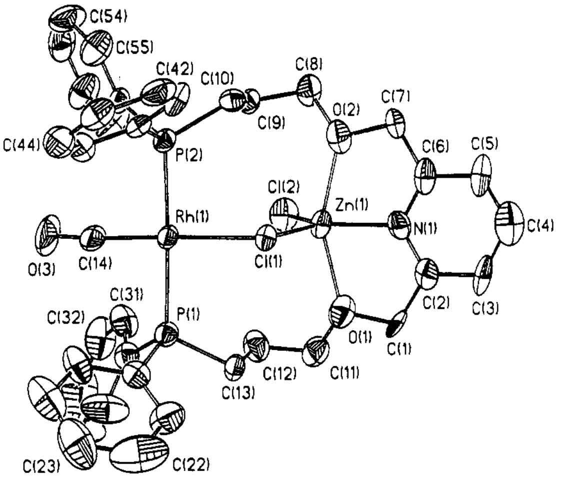

Figure 1. Structure of the {**2**[ZnCl(μ-Cl)Rh(CO)]}$^+$ cation showing the 40% probability thermal ellipsoids and atom-labeling scheme. The $CF_3SO_3^-$ anion and three C_6H_6 solvent molecules (all are noninteracting with the cation) and hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg) are as follows: Rh(1)–P(1), 2.331 (5); Rh(1)–P(2), 2.325 (4); Rh(1)–C(14), 1.84 (2); Rh(1)–Cl(1), 2.399 (4); C(14)–O(3), 1.11 (2); Rh(1)–Zn(1), 4.002 (1); Zn(1)–O(1), 2.22 (1); Zn(1)–O(2), 2.23 (1); Zn(1)–N(1), 2.00 (1); Zn(1)–Cl(1), 2.360 (4); Zn(1)–Cl(2), 2.201 (6); P(1)–Rh(1)–P(2), 174.0 (2); C(14)–Rh(1)–Cl(1), 176.1 (7); P(1)–Rh(1)–Cl(1), 91.4 (2); Cl(1)–Rh(1)–P(2), 89.8 (2); P(2)–Rh(1)–C(14), 90.7 (5); P(1)–Rh(1)–C(14), 87.7 (5); Rh(1)–Cl(1)–Zn(1), 114.5 (2); Rh(1)–C(14)–O(3), 175.2 (2); O(1)–Zn(1)–O(2), 151.3 (5); Cl(1)–Zn(1)–Cl(2), 120.3 (2); Cl(1)–Zn(1)–N(1), 107.9 (4); Cl(1)–Zn(1)–O(1), 89.9 (3); Cl(1)–Zn(1)–O(2), 92.7 (3); Cl(2)–Zn(1)–O(1), 102.8 (4); Cl(2)–Zn(1)–O(2), 100.5 (3); C(12)–Zn(1)–N(1), 131.9 (4); N(1)–Zn(1)–O(1), 75.5 (5); N(1)–Zn(1)–O(2), 76.5 (5).

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[7] Compound **3**: A solution of **2** (0.913 g, 1.54 mmol) in 10 mL of CH_2Cl_2 was added to a suspension of $Zn(O_3SCF_3)_2$[6] (0.645 g, 1.77 mmol) in 30 mL of CH_2Cl_2 under N_2. After it was stirred for 0.5 h, the solution was filtered and the CH_2Cl_2 removed under reduced pressure. The remaining white solid was washed with hexanes and dried in vacuo to give **3** in 92% yield. ^{1}H NMR (CD_2Cl_2, TMS): δ 8.07 (t, 1H, 4-py), 7.43 (m, 22H, 3,5-py, Ph), 5.00 (s, 4H, py–CH_2–O), 4.04 (t, 4H, OCH_2CH_2), 2.31 (m, 4H, CH_2PPh_2), 1.87 (m, 4H, $CH_2CH_2CH_2$). $^{31}P\{^1H\}$ NMR (CH_2Cl_2, external H_3PO_4): δ −9.5.

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[9] Compound **4**: All operations were performed under an Ar atmosphere. A solution of [Bu_4N][$RhCl_2(CO)_2$][8] (284 mg, 0.601 mmol) in 20 mL of CH_2Cl_2 was added to a well-stirred solution of **3** (573 mg, 0.600 mmol) in 40 mL of CH_2Cl_2. After 0.5 h, the CH_2Cl_2 was removed under reduced pressure, and the solid yellow residue redissolved in 20 mL of warm CH_2Cl_2. After the solution volume was reduced to ca. 5 mL using an Ar purge, the solution was cooled to 0 °C. A bright yellow solid crystallized and was isolated by filtration. The solid was washed with a minimum volume of cold CH_2Cl_2 and dried in vacuo to give **4** in 60% yield. ^{1}H NMR (CD_2Cl_2, TMS): δ 8.10 (t, 1H, 4-py), 7.67 (m, 8H, Ph), 7.52 (d, 2H, 3,5-py), 7.48 (m, 12H, Ph), 5.00 (s, 4H, py–CH_2–O), 4.05 (s, 4H, OCH_2CH_2), 2.78 (m, 4H, CH_2PPh_2), 2.29 (m, 4H, $CH_2CH_2CH_2$). $^{31}P\{^1H\}$ NMR (CH_2Cl_2, external H_3PO_4): δ +26.4 (d, J_{Rh-P} = 119 Hz). IR (ν_{CO}, cm^{-1}): 1995, CH_2Cl_2; 1982, fluorocarbon mull.

[10] X-ray data for $C_{38}H_{39}NO_6F_3P_2SRhZn\cdot 3C_6H_6$: monoclinic, space group $C2/c$, with a = 28.87 (1) Å, b = 13.743 (4) Å, c = 31.82 (1) Å, β = 104.17 (3)°, V = 12 239 (7) Å^3, ρ(calcd) = 1.348 g/cm^3, Z = 8, μ = 9.17 cm^{-1}, and $R(F)$ = 9.07%. Of 8491 data collected (Nicolet R3m, 293 K, Mo Kα) and systematically present, 4083 were observed. Three molecules of benzene for each Zn/Rh complex were located in the lattice; these and the phenyl substituents were constrained to rigid, planar hexagons. The triflate anion was severely disordered; only the S atom was reliably located. Modeling failed to produce a chemically rational structure for the anion. All non-hydrogen cation atoms, solvate atoms, and the triflate S and F atoms were refined anisotropically. Other triflate centers of electron density were refined as isotropic oxygen atoms.

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the methylene protons adjacent to the N and O atoms of **4** is virtually identical with that found in **3**, indicating that the Zn(II) ion remains fixed in the ONO chelating site.

To correlate the structure of these heterobinuclear complexes with reactivity, we have also been studying the hydroformylation[20] of a series of functionalized terminal olefins of varying chain length (e.g. 1-hexene, 5-hexen-1-ol, propene, and 2-propen-1-ol) using both the {**2**[ZnCl(μ-Cl)Rh(CO)]}$^+$ cation, as its BF_4^- salt,[21] and RhCl(CO)$(PPh_3)_2$[22] as catalysts. Preliminary results indicate that the rates are slightly slower for the heterobinuclear complex than for the mononuclear species and that there is no significant difference in substrate selectivity. However, a notable difference was observed in the induction periods for initiation of hydroformylation for the two complexes. While the heterobinuclear complex exhibited no induction period in any of the reactions, the mononuclear complex displayed induction periods of 2–3 h under the same reaction conditions. For the mononuclear complex, this has been attributed to the time required to convert the chloro complex to the active hydrido form.[20] The lack of an induction period in the heterobinuclear-catalyzed reactions can be ascribed to the presence of the coordinated Zn(II) ion, which functions as an internal acceptor removing the chloride ion from the coordination sphere of the Rh(I) center during formation of the active hydrido–rhodium catalyst.[23] This cooperative role for the coordinated Zn(II) ion is supported by the fact that induction periods were also observed when equimolar amounts of the mononuclear Rh catalyst and a mononuclear Zn complex of **2** were both present independently in the hydroformylation reaction mixtures. Future studies will be directed toward exploring the reactivity of this and related halide-free heterobinuclear complexes.

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Supplementary Material Available: Tables of atomic coordinates and isotropic thermal parameters, bond lengths, bond angles, anisotropic thermal parameters, and H atom coordinates (7 pages). Ordering information is given on any current masthead page.

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(21) The BF_4^- salt was prepared by the same method as for **4** from **2** and $[Zn(CH_3CN)_4][BF_4]_2$.[25] Elemental analysis supports the formulation {**2**[ZnCl(μ-Cl)Rh(CO)]}(BF_4). Anal. Calcd for $C_{38}H_{39}NO_3P_2BCl_2F_4RhZn$: C, 48.26; H, 4.16; N, 1.48; O, 5.07; P, 6.5; B, 1.1; Cl, 7.50; F, 8.03; Rh, 10.88; Zn, 6.91. Found: C, 48.84; H, 4.20; N, 1.57; O, 5.54; P, 6.2; B, 1.1; Cl, 7.15; F, 7.37; Rh, 9.9; Zn, 6.4.

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