Carbonylation of Ethene to Acrolein in the Presence of the Early–Late Heterobimetallic Complex $[AsPh_4][(\eta^5\text{-}C_5Me_5)_2Zr(\mu\text{-}S)_2Rh(CO)_2]\cdot THF$

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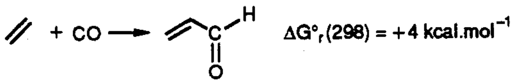
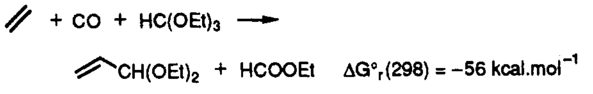
Summary: The $[AsPh_4][(\eta^5\text{-}C_5Me_5)_2Zr(\mu\text{-}S)_2Rh(CO)_2]$ complex has been prepared and fully characterized by an X-ray crystal structure analysis. In the presence of triphenylphosphine it initiates the carbonylation of ethene to give acrolein; upon addition of triethyl orthoformate the reaction is catalytic.

The use of transition metal complexes to effect direct functionalization of raw chemicals through C–H activation appears to be a very attractive target since recent studies have shown that stoichiometric reactions can be carried out and rationalized, in terms of fundamental steps, within the coordination sphere of the metal.[1]

We report here the direct carbonylation of ethene to acrolein (eq 1) via a homogeneous process involving the early–late bimetallic complex $[AsPh_4][Cp^*_2Zr(\mu\text{-}S)_2Rh(CO)_2]$ (1). Moreover, in the presence of triethyl orthoformate, in order to have favorable thermodynamic conditions, the reaction (eq 1) has been found to be catalytic (eq 2).[2]



(1)



(2)

As the C–H activation reactions presently observed in homogeneous conditions involve stoichiometric processes either on early metal complexes or on electron-rich late metal centers,[1] a heterobimetallic compound has been designed with the aim of reaching a catalytic carbonylation. Such a cooperative effect between different metals has recently been demonstrated by Stephan for the hydroformylation of hex-1-ene.[3]

The anionic complex 1 was prepared[4] in 75% yield by addition of $[Cp^*_2Zr(SH)_2]$[5] (2, $Cp^* = \eta^5\text{-}C_5Me_5$) to $[AsPh_4][RhCl_2(CO)_2]$[6] (3). An X-ray structure analysis of 1 was performed. The anionic molecular unit is shown in Figure 1.[7] Zirconium and rhodium metal centers are associated through two sulfur bridges, the Rh–Zr distance being 3.161(3) Å. The zirconium atom is in a tetrahedral environment, whereas the rhodium atom presents a square-planar arrangement. The ZrS_2Rh core is almost planar. This complex was also characterized by elemental analysis, infrared, and NMR.[8] Two ν_{CO} bands with a 70-cm^{-1} separation are characteristic of two geminal CO ligands. In ^1H and ^{13}C NMR spectra, the Cp* and CO ligands and the $AsPh_4^+$ counterion were detected together with the THF molecule present in the cell.

Provided a 5-fold excess of triphenylphosphine is added, complex 1 reacts at 140 °C with ethene (1 MPa) and carbon monoxide (1 MPa) during 16 h to give acrolein[9] (eq 1). This reaction is substoichiometric[10] (0.4 mol with respect to 1), but by addition of triethyl orthoformate to the reaction medium, 2 mol of 3,3-diethoxyprop-1-ene per mole of complex 1 was obtained, giving rise to a catalytic reaction. Indeed, triethyl orthoformate allows ΔG°_r to have a largely negative value and affords the protected form of acrolein in the acetal function (eq 2). This acetal was easily characterized by GC/MS.[11]

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(1) Leading references: (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352; **1983**, 105, 3929. (b) Wax, M. J.; Stryker, J. M.; Buchanan, J. M.; Kouac, C. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 1121. (c) Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 7190. (d) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491. (e) See also: Hill, G. L. *Activation and functionalization of alkanes*; J. Wiley and Sons: New York, 1989.

(2) Stull, D. R.; Westrum, E. F.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Kreiger: FL, 1987.

(3) Gelmini, L.; Stephan, D. W. *Organometallics* **1988**, *7*, 849.

(4) To a THF solution of 0.163 mmol of 2 was added at room temperature a THF solution containing 0.163 mmol of 3 and 1.63 mmol of triethylamine. Filtration to remove $[NHEt_3]Cl$, followed by concentration under reduced pressure and repeated washings with toluene to eliminate byproducts, mainly $[Cp^*_2ZrCl_2]$ (Manriquez, J. M.; MacAlister, D. E.; Rosenberg, E.; Shiller, A. M.; Williamson, K. L.; Chan, S. I.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 3078), small amounts of $[Cp^*_2Zr(OH)(SH)]$ and $[Cp^*_2Zr(OH)_2]$ (Hilhouse, G. L.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5472), and a compound which is probably $[AsPh_4][Rh(SH)_2(CO)_2]$, led to a pure yellow residue of 1 in 75% yield. From a THF/pentane mixture yellow crystals were grown. A few nontwinned crystals of modest quality were obtained.

(5) $[Cp^*_2Zr(SH)_2]$ was prepared by a procedure similar to that published for $[Cp_2Zr(SH)_2]$: McCall, J. M.; Shaver, A. *J. Organomet. Chem.* **1980**, *193*, C37.

(6) Preparation of $[AsPh_4][RhCl_2(CO)_2]$ was first performed by A. Thorez and R. Poilblanc (Thorez, A. Thèse 3ème cycle, Université Paul Sabatier, 1979) by addition of $AsPh_4Cl$ to $[Rh_2Cl_2(CO)_4]$. For our part, we prepared directly the species $H[RhCl_2(CO)_2]$ (Vallarino, L. M. *Inorg. Chem.* **1965**, *4*, 161) to which we added $AsPh_4Cl$.

(7) Crystal data for $C_{50}H_{58}AsO_3RhS_2Zr$ (1): yellow crystal, orthorhombic, $P2_12_12_1$ (No. 19), $a = 12.113(5)$ Å, $b = 17.690(3)$ Å, $c = 22.478(4)$ Å, $V = 4816.6$ Å^3, $Z = 4$. Of 3870 reflections collected ($T = 296$ K, $2\theta_{max} = 40°$), 1656 were considered observed and used ($I > 1\sigma(I)$). The structure was solved and refined by Patterson, difference Fourier, and least-squares methods. The Zr, Rh, S, As, C, and O (carbonyl) atoms were refined with anisotropic temperature factors, but all other carbon and oxygen atoms were isotropic. $R = 6.4\%$ and $R_w = 6.5\%$, GOF = 1.597, and the largest peaks in the final difference Fourier have heights of −0.55 and +0.63 e/Å^3.

(8) Key infrared and NMR data for 1. Infrared: 2003 (vs), 1933 (vs) cm^{-1} (ν_{CO}). ^1H NMR (C_6D_6): δ 1.4 (m, THF, 2H), 2.15 (s, Cp*, 30H), 3.5 (m, THF, 2H), 7.2 (m, Ph, 20H). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 13.91 (s, $(CH_3)_5C_5$), 25.81 (q, THF), 67.88 (q, THF), 115.20 (s, $(CH_3)_5C_5$), 129.92 (s, Ph, C_1), 132.58 (s, Ph, C_3 and C_5), 134.74 (s, Ph, C_2 and C_6), 135.96 (s, Ph, C_4), 192.50 (d, $J_{Rh-C} = 71.$, CO). Anal. Calcd for $C_{50}H_{58}O_3ZrRhS_2As$: C, 57.73; H, 5.62; O, 4.61; Zr, 8.77; Rh, 9.89; S, 6.17; As, 7.20. Found: C, 57.64; H, 5.52; Zr, 9.17; Rh, 10.15; S, 6.22; As, 7.56.

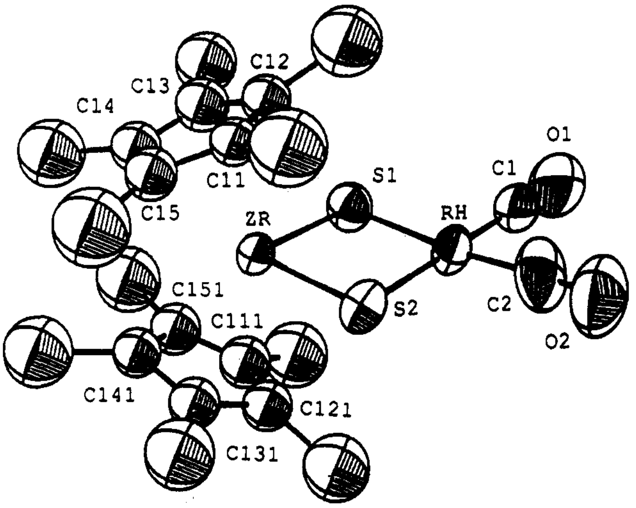

Figure 1. ORTEP drawing of the structure of [AsPh$_4$]-[(Cp*)$_2$Zr(μ-S)$_2$Rh(CO)$_2$]·THF (1). Selected bond lengths (Å) and bond angles (deg): Zr–Rh = 3.161(3), Zr–S(1) = 2.413(9), Zr–S(2) = 2.428(8), Rh–S(1) = 2.378(8), Rh–S(2) = 2.367(8), Rh–C(1) = 1.88(3), Rh–C(2) = 1.75(4), Zr–C(11) = 2.61(3), Zr–C(12) = 2.61(3), Zr–C(13) = 2.59(4), Zr–C(14) = 2.60(3), Zr–C(15) = 2.61(3), Zr–C(111) = 2.63(3), Zr–C(121) = 2.61(3), Zr-C(131) = 2.59(3), Zr–C(141) = 2.59(3), Zr–C(151) = 2.58(3), As–C(31) = 1.88(2), As–C(41) = 1.79(3), As–C(51) = 1.90(2), As–C(61) = 1.93(3); S(1)–Zr–S(2) = 96.1(3), S(1)–Rh–S(2) = 98.8(3), Rh–C(1)–O(1) = 177(3), Rh–C(2)–O(2) = 172(3), S(1)–Rh–C(1) = 82.0(9), S(1)–Rh–C(2) = 173(1), S(2)–Rh–C(1) = 178.6(9), S(2)–Rh–C(2) = 87(1), C(1)–Rh–C(2) = 92.(2), Zr–S(1)–Rh = 82.5(3), Zr–S(2)–Rh = 82.5(3), C(31)–As–C(41) = 109(1), C(31)–As–C(51) = 111(1), C(31)–As–C(61) = 108(1), C(41)–As–C(51) = 111(1), C(41)–As–C(61) = 109(1), C(51)–As–C(61) = 109(1), As–C(31)–C(32) = 119(2), As–C(31)–C(36) = 122(2), As–C(41)–C(42) = 120(2), As–C(41)–C(46) = 125(3), As–C(51)–C(52) = 123(2), As–C(51)–C(55) = 120(2), As–C(61)–C(62) = 119(2), As–C(61)–C(66) = 118(3).

In order to understand the intimate role played by each metal center in complex 1, related zirconium and rhodium complexes were studied separately in the reaction involving ethene and carbon monoxide. The rhodium precursors 3 and [Rh$_2$(μ-S-*t*-Bu)$_2$(CO)$_4$] (4),[12] which is reminiscent of 1 because of the two sulfur bridging atoms, were found to be totally inactive both in the presence or in the absence of triphenylphosphine. Similarly, complex 2 without any extra ligand not only was inactive but also decomposed to give 1 equiv of Cp*H and 1 equiv of fulvalene 5[13] resulting from a CH$_3$ activation of the Cp* ligand on the zirconium center. However, addition of a slight excess of triphenylphosphine to complex 2 (ratio 5/1) led to the production of 0.2 mol (per mole of 2) of acrolein in the gas phase. On the other hand, the solution contained 1.8 mol of Cp*H and only 0.2 mol of 5, as analyzed by GC/MS. Black zirconium- and sulfur-containing materials were found at any time simultaneously with the formation of equivalent quantities of acrolein and 5.

All these findings can be explained in terms of a multistep mechanism involving three well-documented sequences; activation of ethene on the zirconium center to give vinyl species,[14] insertion of CO into the zirconium–carbon bond[15] leading to acrolein through reductive elimination, and C–H activation of a CH$_3$ group from Cp* [16] followed by decomposition.

In contrast to these results, the reaction of 1 in the presence of PPh$_3$, but in the absence of orthoformate, was characterized by the production of 0.4 mol of acrolein and almost no fulvalene 5, suggesting that the reaction pathway is quite different from that which occurs with complex 2 alone and requires the simultaneous presence of the two rhodium and zirconium centers. As compared to the reactivity of complex 2, the rhodium center seems to direct the carbonylation of ethene which occurs on the zirconium center and to prevent most of the side reactions. Addition of orthoformate (2-fold excess with respect to 1) to the medium makes the reaction catalytic with respect to the bimetallic complex 1. Thus, although only two turnovers were achieved, the catalytic carbonylation of ethene to acrolein involves a bimetallic [Zr–Rh] complex for which the cooperative effect is under investigation.

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Supplementary Material Available: Detailed results of the X-ray crystal structure analysis of [AsPh$_4$][(η^5-C$_5$Me$_5$)$_2$Zr(μ-S)$_2$Rh(CO)$_2$] including tables of experimental data, positional and thermal parameters, general temperature factor expressions (*U*, *B*), bond distances, bond angles, and least-squares planes and structures of [AsPh$_4$][(η^5-C$_5$Me$_5$)$_2$Zr(μ-S)$_2$Rh(CO)$_2$] (8 pages). Ordering information is given on any current masthead page.

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(9) An autoclave was charged with 10^{-5} mol of 1, 5×10^{-5} mol of triphenylphosphine, 10 mL of *n*-hexane, 1 MPa of ethene, and 1 MPa of carbon monoxide. The reaction was performed at 140 °C for 16 h under stirring. After cooling, the autoclave was carefully and slowly depressurized in a trap containing an acidic solution of dinitrophenylhydrazine where acrolein gave an orange precipitate of the corresponding dinitrophenylhydrazone (March, J. *Advanced Organic Chemistry*; J. Wiley: New York, 1988; p 804). This hydrazone was separated, washed, dried, characterized by ^{1}H NMR, and compared to an authentic sample prepared from commercial acrolein added to a solution of dinitrophenylhydrazine.

(10) A total of 0.4 mol of hydrazone was obtained[9] per mol of complex 1. This experiment was reproducible, giving the same product with the same yield.

(11) An autoclave was charged with 2×10^{-4} mol of triethyl orthoformate, 10^{-4} mol of 1, 5×10^{-4} mol of PPh$_3$, 10 mL of *n*-hexane, 1 MPa of ethene, 1 MPa of carbon monoxide, and a standard (4×10^{-4} mol of *n*-octane). The reaction was performed at 140 °C for 16 h under stirring. After cooling, the autoclave was depressurized and the organic solution was analyzed by GC coupled with MS. A total of 2 mol of 3,3-diethoxyprop-1-ene (m/e = 130 amu) per mole of complex 1 was obtained.

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