Fragmentation–Recombination Reactions of the Electron-Rich Binuclear Hydride $[(Pr^i_2PCH_2CH_2CH_2PPr^i_2)Rh]_2(\mu\text{-}H)_2$ with Dibenzylzinc. X-ray Structure of $[(Pr^i_2PCH_2CH_2CH_2PPr^i_2)Rh]_2(\mu\text{-}H)_2(\mu\text{-}ZnCH_2Ph)_2$

Michael D. Fryzuk,*,† **David H. McConville, and Steven J. Rettig**‡

Department of Chemistry, University of British Columbia
2036 Main Mall, Vancouver, BC, Canada V6T 1Y6

Received January 16, 1990

Summary: The reaction of $Zn(CH_2Ph)_2$ with $[(dippp)Rh]_2(\mu\text{-}H)_2$ generates two rhodium-containing products, $(\eta^3\text{-}CH_2Ph)Rh(dippp)$ and the tetranuclear derivative $[(dippp)Rh]_2(\mu\text{-}H)_2(\mu\text{-}ZnCH_2Ph)_2$, the latter presumably via initial oxidative addition of a zinc benzyl moiety and unsymmetrical fragmentation to mononuclear species followed by recombination and loss of H_2.

One of the methods[1] used to generate transition-metal-to-zinc bonds is the reaction of a transition-metal hydride complex (HML_n) with a diorganozinc derivative via elimination[2] of a hydrocarbon (eq 1). This appears

$$L_nMH + ZnR_2 \rightarrow L_nM\text{-}ZnR + RH \qquad (1)$$

to be a fairly general reaction for most mononuclear metal hydrides and is only complicated by disproportionation[3] type reactions to generate symmetrical products. The symmetrization reaction can be avoided by the use of polyhapto[4] organozinc reagents such as $ZnCp_2$ (Cp = η^5-C_5H_5). For example, reaction of Cp_2NbH_3 with $ZnEt_2$[5] leads to the formation of the symmetrical dimer $[Cp_2NbH_2]_2Zn$, whereas reaction of this same niobium complex with $ZnCp_2$[2] generates the mononuclear, unsymmetrical derivative Cp_2NbH_2ZnCp.

In an effort to build polynuclear clusters containing bare electropositive metals with only bridging hydrides as ancillary ligands, we have initiated a study on the reactivity of simple organometallic reagents of groups 12 and 13 with a series of electron-rich binuclear hydrides of the type $[(R_2P(CH_2)_nPR_2)Rh]_2(\mu\text{-}H)_2$. In this paper we report our initial results on the reaction of dibenzylzinc with the rhodium hydride dimer $[(dippp)Rh]_2(\mu\text{-}H)_2$ (where dippp = 1,3-bis(diisopropylphosphino)propane). What emerges from this work is the facile formation of a tetranuclear product by an apparent fragmentation–recombination sequence, yet again showing the unique behavior of these binuclear rhodium hydrides as compared to that of mononuclear analogues.[6]

The reaction[7] of $[(dippp)Rh]_2(\mu\text{-}H)_2$ (**1**) with 1 equiv of $Zn(CH_2C_6H_5)_2$[8] did not lead to the expected symmetrical complex $[(dippp)Rh]_2Zn$ (by elimination of 2 equiv of toluene) but rather gave two new products in a 1:1 ratio by ^{31}P NMR spectroscopy. The reaction was complete at −80 °C in a matter of minutes, and the two compounds could be separated by fractional crystallization from toluene at −40 °C. The less soluble dark red, crystalline complex **2** was shown to have the molecular formula $Rh_2H_2(ZnCH_2Ph)_2(dippp)_2$ on the basis of spectroscopic and analytical data,[9] and the more soluble pale orange compound **3** was identified[10] as the mononuclear η^3-benzyl derivative $Rh(\eta^3\text{-}CH_2Ph)(dippp)$; when the experiment was carried out in C_6D_6, no toluene was detected in this reaction. The NMR spectral data[9] of **2** are diagnostic of a dimer by the multiplicity and symmetry of the hydride pattern. However, these data did not provide information on the detailed geometry of this material. Therefore, an X-ray crystallographic study[11] of **2** was undertaken to

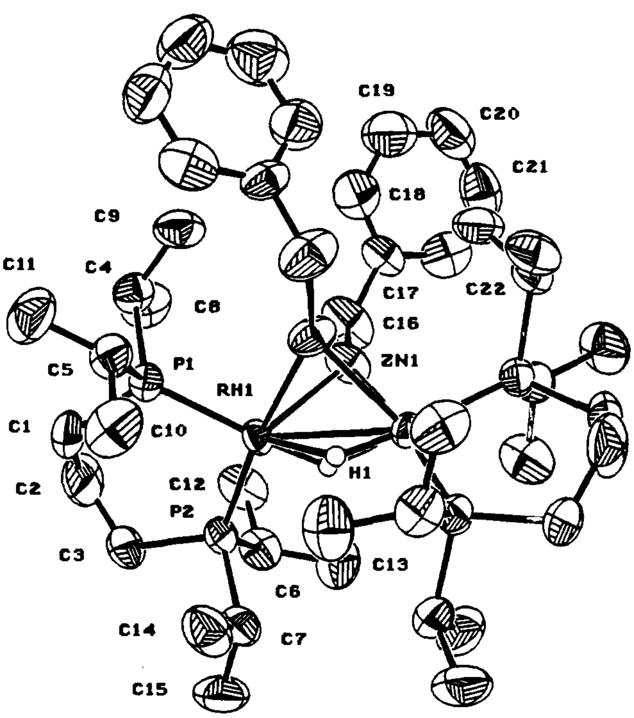


Figure 1. Molecular structure of $[(Pr^i_2PCH_2CH_2CH_2PPr^i_2)Rh]_2(\mu\text{-}H)_2(\mu\text{-}ZnCH_2Ph)_2$ (**2**). Selected bond lengths (Å) and bond angles (deg) are as follows: Rh1-Rh2 = 2.764 (1), Rh1-Zn1 = 2.513 (1), Rh1-Zn2 = 2.558 (1), Rh1-P1 = 2.255 (2), Rh1-P2 = 2.261 (2), Rh1-H1 = 1.8 (1), Rh1-H2 = 1.4 (1); Rh1-Zn1-Rh2 = 66.05 (4), Rh1-H1-Rh2 = 116 (5), P1-Rh1-P2 = 96.12 (7).

---

† E. W. R. Steacie Fellow (1990–1992).

‡ Experimental Officer, UBC Crystal Structure Service.

(1) St. Denis, J. N.; Butler, W.; Glick, M. D.; Oliver, J. P. *J. Organomet. Chem.* **1977**, *129*, 1.

(2) (a) Budzelaar, P. H. M.; den Haan, K. H.; Boersma, J.; van der Kerk, G. J. M.; Spek, A. L. *Organometallics* **1984**, *3*, 156. (b) Budzelaar, P. H. M.; van der Zeijden, A. A. H.; Boersma, J.; van der Kerk, G. J. M.; Spek, A. L.; Duisenberg, A. J. M. *Organometallics* **1984**, *3*, 159.

(3) Budzelaar, P. H. M.; Alberts-Jensen, H. J.; Mollema, K.; Boersma, J.; van der Kerk, G. J. M. *J. Organomet. Chem.* **1983**, *243*, 137.

(4) Budzelaar, P. H. M.; Boersma, J.; van der Kerk, G. J. M. *J. Organomet. Chem.* **1980**, *202*, C71.

(5) Tebbe, F. N. *J. Am. Chem. Soc.* **1973**, *95*, 5412.

(6) (a) Fryzuk, M. D.; Piers, W. E. *Polyhedron* **1988**, *7*, 1001. (b) Fryzuk, M. D.; Piers, W. E. *Organometallics*, in press. (c) Fryzuk, M. D.; Piers, W. E.; Rettig, S. J.; Jones, T.; Einstein, F. W. B.; Albright, T. S. *J. Am. Chem. Soc.* **1989**, *111*, 5709.

(7) In a typical reaction 0.048 g (0.194 mmol) of $Zn(CH_2C_6H_5)_2$ dissolved in 5 mL of toluene was added dropwise with stirring to 0.148 g (0.194 mmol) of $[(dippp)Rh]_2(\mu\text{-}H)_2$ dissolved in 10 mL of toluene. The solution was concentrated to 5 mL and cooled to −40 °C, yielding 0.085 g of $Rh_2H_2(ZnCH_2Ph)_2(dippp)_2$ (41% based on $[(dippp)Rh]_2(\mu\text{-}H)_2$). Further concentration of the solution and cooling gave 0.057 g of $Rh(\eta^3\text{-}CH_2Ph)(dippp)$ (31% based on $[(dippp)Rh]_2(\mu\text{-}H)_2$).

(8) Schrock, R. R. *J. Organomet. Chem.* **1976**, *122*, 209.

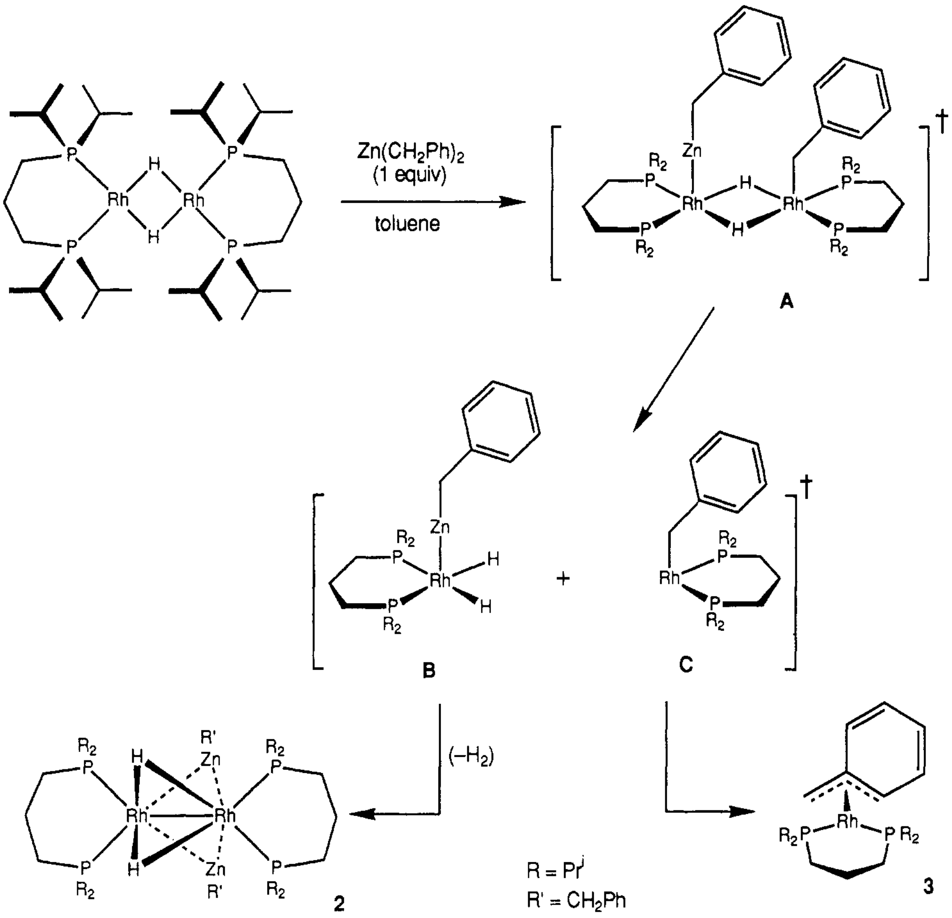
(9) **2**: ^1H NMR (C_6D_6, 25 °C) δ 7.25–6.95 (m, 10 H, Ph), 2.33 (s, 4 H, CH_2Ph), 1.68–0.93 (m, 68 H, ligand resonances), −9.38 ppm (m, 2 H, H_b); $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C, external reference $P(OMe)_3$ at 141.0 ppm) δ 46.6 (d, 4 P, $J_{P\text{-}Rh}$ = 154 Hz). Anal. Calcd (found) for $C_{44}H_{84}P_4Rh_2Zn_2$: C, 49.22 (49.07); H, 7.88 (7.73).

(10) **3**: ^1H NMR (C_6D_6,25 °C): δ 7.24 (t, 2 H, H_m), 6.63 (t, 1 H, H_p), 5.87 (d, 2 H, H_o), 2.26 (d, 2 H, CH_2Ph), 1.91–0.83 (m, 34 H, ligand resonances); $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C, external reference $P(OMe)_3$ at 141.0 ppm) δ 48.4 (dd, 1 P, $J_{P\text{-}Rh}$ = 242 Hz, $J_{P\text{-}P'}$ = 41 Hz), 34.1 (dd, 1 P, $J_{P\text{-}Rh}$ = 172 Hz, $J_{P\text{-}P}$ = 41 Hz). Anal. Calcd (found) for $C_{22}H_{41}P_2Rh$: C, 56.17 (56.08); H, 8.78 (8.77).

(11) Red crystals of **2** were obtained from concentrated toluene solutions at −40 °C: $C_{44}H_{84}P_4Rh_2Zn_2$, M_r 1073.6, monoclinic, space group $C2/c$, a = 19.608 (7) Å, b = 12.891 (6) Å, c = 22.847 (6) Å, β = 120.02 (2)°, V = 5001 (3) Å^3, Z = 4, D_{calcd} = 1.426 g cm^{-3}, $F(000)$ = 2232 e, T = 294 K, graphite-monochromated Mo Kα radiation, λ = 0.71069 Å, μ(Mo Kα) = 17.65 cm^{-1}, R = 0.044, R_w = 0.048 for 2773 independent reflections with $I > 3.00\sigma(I)$.

0276-7333/90/2309-1359$02.50/0

Scheme I



determine its structure and the nature of the bonding in the complex. The results of this study are shown in Figure 1 along with some important bond lengths and bond angles.

The dimeric structure consists of two (dippp)Rh fragments bridged by two $ZnCH_2Ph$ units and two hydrides, which were located in the final difference Fourier map. The two rhodium atoms and two zinc atoms occupy the four corners of a distorted tetrahedron. It is notable that this tetranuclear rhodium–zinc derivative would be considered as an *unsymmetrical* transition-metal–zinc complex because of the organic group still bonded to the zinc center. Attempts to induce disproportionation by heating solutions of **2** to +80 °C failed; the starting complex could be recovered unchanged in virtually quantitative yield.

The NMR spectral data of **3** were characteristic of an η^3-benzyl complex undergoing rapid (at room temperature) suprafacial shifts,[12] since the benzylic protons are equivalent as are the phenyl ortho protons and the meta hydrogens. This same material could be obtained from the reaction of the chloride dimer $[(dippp)Rh]_2(\mu\text{-}Cl)_2$ with $Zn(CH_2Ph)_2$ in >90% yield.

The reaction of $[(dippp)Rh]_2(\mu\text{-}D)_2$ with 1 equiv of $Zn(CH_2Ph)_2$ results in the formation of $[(dippp)Rh]_2(\mu\text{-}D)_2(\mu\text{-}ZnCH_2Ph)_2$ (**2**-d_2) only. There was no detectable deuterium incorporation in the η^3-benzyl unit of **3**. A possible mechanism consistent with the deuterium-labeling experiment and product analysis is shown in Scheme I.

Oxidative addition[13] of the Zn–C bond across the rhodium hydride core of $[(dippp)Rh]_2(\mu\text{-}H)_2$ would generate the trinuclear derivative A; upon asymmetric cleavage of A, there would be generated the Rh(III) and Rh(I) fragments B and C, respectively. The Rh(III) fragment B must be fairly reactive, since no evidence of this moiety was observed even at −80 °C. Dimerization of B followed by (or concomitant with) the loss of H_2 completes the formation of **2**. Alternatively, fragment B could conceivably lose H_2 to give a monomeric rhodium–zinc benzyl complex and then recombine with another fragment B to give the tetranuclear derivative **2**. In any case, the ratio of the products **2**:**3** was always found to be 1:1 over a wide range of stoichiometries and temperatures. The Rh(I) fragment C must isomerize to the η^3 form, which presumably stabilizes an otherwise reactive Rh(I), 14e complex.

We are currently attempting to extend this mode of reactivity to other dialkylzinc reagents that can form stable Rh(I) fragments as well as to the group 13 derivatives which may undergo a similar mode of reactivity. Transformations of this unusual rhodium–zinc tetranuclear species are also underway; the possibility that a catalytic hydrozincation process can be developed is being pursued.

Acknowledgment. Financial support for this work was provided by the NSERC (operating grants to M.D.F. and postgraduate scholarship to D.H.M.). We also thank Johnson Matthey for the generous loan of $RhCl_3$.

Supplementary Material Available: Listings of experimental details, final atomic coordinates, calculated hydrogen atom positions, anisotropic thermal parameters, bond lengths, bond angles, and least-squares planes for **2** (13 pages); a listing of observed and calculated structure factors for **2** (39 pages). Ordering information is given on any current masthead page.

---

[12] Cotton, F. A.; Marks, T. J. *J. Am. Chem. Soc.* **1969**, *91*, 1339.

[13] Budzelaar, P. H. M.; Boersma, J.; van der Kerk, G. J. M.; Spek, A. L.; Duisenberg, A. J. M. *Organometallics* **1985**, *4*, 680.