counted for the low yields.[23] Its ^1H and ^{13}C NMR spectra[24] reveal that compound **3** contains a η^5-pentadienyl group but in unsymmetric environments. Despite vigorous efforts in crystallization of **3**, an X-ray diffraction study[25] of **3** was hampered by its poor crystallinity. Of the two possible structures η^5-S and η^5-U shapes, the former is more likely

η^5-S

η^5-U

for **3** from the comparison of its ^1H NMR chemical shifts[26] to those of (η^5-*trans*-pentadienyl)$Fe(CO)_3^+$ and related cations.[27] In particular, the resonances of H^1 (δ 1.22) and H^5 (δ 1.55), which lie more upfield than other proton resonances, are characteristic of the two anti protons on the "butadiene" mouth of the ligand. Moreover, all reported unsymmetric η^5-U-type compounds[28] are prone to undergo rotation of the pentadienyl group at ambient temperatures. Such a process however is not observed for **3** even at 110 °C from the ^1H NMR studies (toluene-d_8). Ernst and co-workers[2d] have recently reported the structures of the related compounds $[2,4\text{-}(CH_3)_2C_5H_5]_2M(PEt_3)$ (M = Mo, Nb, Zr). For molybdenum complex, the two pentadienyl groups exist, respectively, in η^5-S and symmetric η^5-U forms; and for niobium and zirconium analogues, both ligands have the symmetric η^5-U structures. The metal sizes and electronic influences of molybdenum are thought to be the key factors in adoption of the unusual "S" configurations.

The ν(CO) band of **3** is observed at 1924 (s) cm^{-1}, significantly higher than that at 1868 (s) cm^{-1} for $Cp_2Mo(CO)$.[9b] The pentadienyl ligand appears to withdraw more electron density from the molybdenum center than the cyclopentadienyl group. The two compounds however have common aspects in chemical and physical properties. Like $Cp_2Mo(CO)$, **3** is greenish yellow solid extremely soluble in organic solvent and readily sublimes at 40 °C. Upon photolysis, **3** loses the CO group to give a red precipitate of undetermined composition. $Cp_2Mo(CO)$ forms the very reactive species "Cp_2Mo" in photolytic reactions. Experimental evidence to prove the existence of its pentadienyl analogue, the 16e "$(C_5H_5)Mo(C_5H_7)$", is underway.

Acknowledgment. We wish to thank the National Science Council, ROC, for financial support of this work.

Registry No. 1, 104293-11-0; 2 (exo isomer), 104293-12-1; 2 (endo isomer), 104418-74-8; 3, 104293-13-2; $CpMo(CO)_3Na$, 12107-35-6; *trans*-1-chloropenta-2,4-diene, 28070-18-0.

Supplementary Material Available: Tables of bond distances and angles, final fractional coordinates, and thermal parameters (3 pages); a listing of observed and calculated structure (23 pages). Ordering information is given on any current masthead page.

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(23) In a blank test, a vacuum-sealed NMR tube containing minor amount (~5 mg) of **3** in toluene-d_8 was irradiated by a 400-W mercury lamp which slowly deposited red insoluble solid during photolysis. The ^1H NMR resonances characteristic of **3** completely vanished after irradiation for 10 h.

(24) Anal. Calcd for $C_{11}H_{12}MoO$: C, 51.57; H, 4.69. Found: C, 51.50; H, 4.65. Mass spectrum (12 eV, ^{98}Mo 23.78%, *m/e*): 258 (M^+). IR spectrum (pentane): ν(CO) 1924 (s) cm^{-1}. ^1H NMR spectrum (400 MHz, benzene-d_6, 23 °C): δ 1.22 (dd, 1 H, H^1), 1.55 (m, 1 H, H^5), 1.76 (d, 1 H, H^7), 2.13 (d, 1 H, H^6), 2.42 (dd, 1 H, H^2), 2.78 (t, 1 H, H^4), 4.15 (m, 1 H, H^3), 4.58 (s, 5 H, C_5H_5), J_{12} = 2.5 Hz, J_{13} = 9.4 Hz, J_{23} = 6.8 Hz, J_{34} = J_{45} = 5.1 Hz, J_{56} = 5.0 Hz, J_{57} = 8.4 Hz, J_{67} = 0 Hz. ^{13}C NMR spectrum (100.6 MHz, 23 °C, benzene-d_6): δ 36.2, 40.1 (CH^1H^2 and CH^6H^7), 69.0, 75.8, 84.8 (CH^3, CH^4, and CH^5), 88.62 (C_5H_5), 239.4 (CO).

(25) Only preliminary data were obtained: space group *Pmma* with a = 10.024 (5) Å, b = 6.58 (2) Å, and c = 17.25 (2) Å. The crystal used for data collection was multiple. A total of 1084 independent reflections with $0° < 2\theta < 50°$ were collected by using the θ–2θ scanning technique; 318 reflections with $I > 2\sigma(I)$ were used. The molybdenum was located at 0.265, 0.356, 0.114 by Patterson synthesis, and the structure factor calculation based on the position of Mo gave R = 33%. The subsequent Fourier map indicated the disorder of the molecule.

(26) For **3**, the value of J_{45} is about 5 Hz, somewhat smaller than the expected value from the trans proton coupling. It is noteworthy that in the related compound $[2,4\text{-}(CH_3)_2C_5H_5]_2Mo(PEt_3)$[2d] the pentadienyl moiety is quite nonplanar. We believe that the distoriton from planarity will lead to a small value of J_{45}.

(27) (a) Sorenson, T. S.; Jablonski, C. R. *J. Organomet. Chem.* **1970**, *25*, C62. (b) Lillya, C. P.; Sahajian, R. A. *Ibid.* **1970**, *25*, C67. (c) Clinton, N. A.; Lillya, C. P. *J. Chem. Soc., Chem. Commun.* **1968**, 579; *J. Am. Chem. Soc.* **1970**, *92*, 3065.

(28) (a) Liu, J.-Z.; Ernst, R. D. *J. Am. Chem. Soc.* **1982**, *104*, 3737. (b) Wilson, D. R., Dilullo, A. A., Ernst, R. D. *Ibid.* **1980**, *102*, 5929. (c) Stahl, L.; Ernst, R. D. *Organometallics* **1983**, *2*, 1229. (d) Williams, G. M.; Fisher, R. A.; Heyn, R. D. *Ibid.* **1986**, *5*, 818.

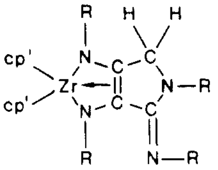
Multiple Insertion and C–C Coupling of Isocyanides: Reaction of Bis(η^5-methylcyclopentadienyl)zirconium Dihydride with Isocyanides

Jeffrey R. Bocarsly,[†] **Carlo Floriani,***[†,§]
Angiola Chiesi-Villa,[‡] **and Carlo Guastini**[‡]

Chemistry Department, Columbia University
New York, New York 10027
and Istituto di Strutturistica Chimica, Centro di Studio
per la Strutturistica Diffrattometrica del CNR
Università di Parma, 43100 Parma, Italy

Received May 20, 1986

Summary: Reaction of *tert*-butyl isocyanide and cyclohexyl isocyanide with bis(η^5-methylcyclopentadienyl)zirconium dihydride led to multiple insertions into the Zr–H bond and to simultaneous reductive coupling of isocyanides with the formation of an unusual zirconacycle:



Current interest in the reduction of carbon monoxide has led to studies of the reactivity of CO with various zirconocene hydrides which have resulted in the observation of C–C bond formation.[1a,b] as well as simple CO reduction by these complexes.[1c] Examination of the reactivity of zirconocene hydrides has recently been extended to reactivity with isocyanides, which are isoelectronic with CO.[2] Specifically, interest has focused on the question of whether CO insertion into a Zr–H bond is thermodynamically feasible and, by analogy, whether such a process occurs in the cp_2ZrH_2–isocyanide system.

Another aspect of this chemistry concerns the role that the cp ligand plays. It has been noted that alkyl substituents on the cp ring increase the ligand to metal electronic donation, thereby heightening metal basicity.[3]

[†] Columbia University.

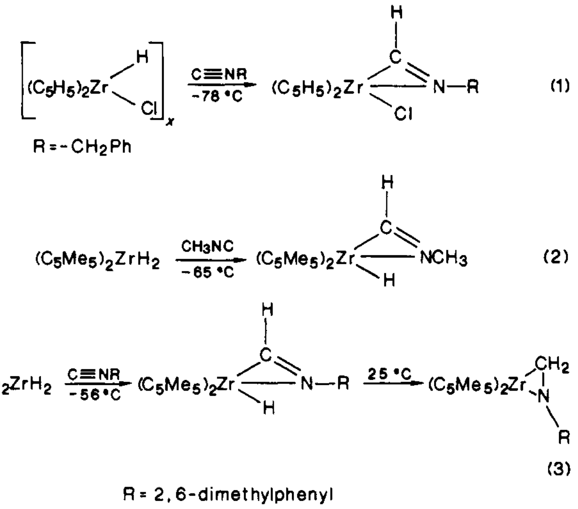
[‡] Università di Parma.

[§] To whom correspondence should be addressed at ICMA, Universitê de Lausanne, 3, Place du Chateau, CH-1005 Lausanne, Switzerland.

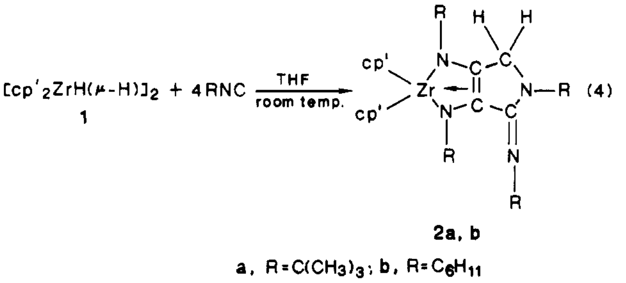
(1) (a) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121–127. (b) Erker, G. *Ibid.* **1984**, *17*, 103–109. (c) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1983**, *105*, 1690–1691.

(2) (a) Frömberg, W.; Erker, G. *J. Organomet. Chem.* **1985**, *280*, 355–363. (b) Wolczanski, P. T.; Bercaw, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 6450–6452.

Recently reported zirconocene-isocyanide chemistry has, in part, attempted to elucidate what difference, if any, substitution on the cyclopentadiene ring entails, via reactions 1–3.[2a,b] These results prompted us to examine the reactivity of isocyanides with $[(C_5H_4Me)_2ZrH(\mu\text{-}H)]_2$ (C_5H_4Me = cp′).[4]



$[cp'_2ZrH(\mu\text{-}H)]_2$ (1) was reacted in a THF suspension at room temperature with increasing amounts of isocyanide until free isocyanide was detected in solution by IR. The final molar ratio of isocyanide to zirconocene hydride was 4:1. Compounds 2 were isolated from solution as bright orange air-sensitive crystals.[5] The products **2a** and **2b** both exhibited a single broad IR absorption above 1600 cm^{-1} [ν = 1637 cm^{-1}, **2a**; ν = 1613 cm^{-1}, **2b**], suggesting the presence of a C=N double bond in the product. The structure of product **2a** was elucidated by an X-ray study on a single crystal.[6]



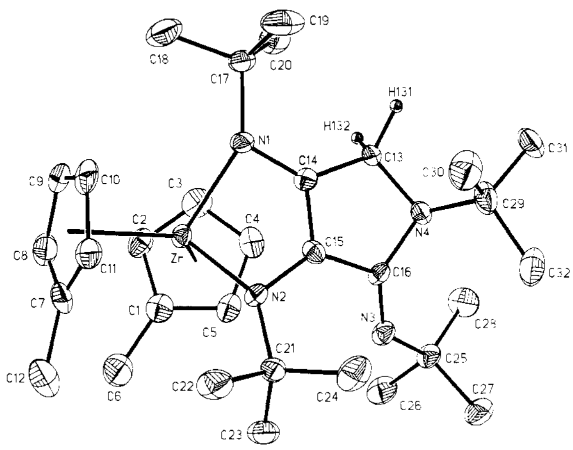


Figure 1. An ORTEP drawing of complex **2a** (30% probability ellipsoids). Bond distances (Å): Zr–N(1), 2.150 (5); Zr–N(2), 2.116 (5); Zr–cp(1), 2.294 (4); Zr–cp(2), 2.295 (4); N(1)–C(14), 1.380 (8); N(2)–C(15), 1.414 (7); C(14)–C(15), 1.386 (9); C(13)–C(14), 1.529 (7); C(13)–N(4), 1.468 (9); N(4)–C(16), 1.430 (8); C(15)–C(16), 1.504 (7); N(3)–C(16), 1.259 (9); Zr–C(14), 2.593 (5); Zr–C(15), 2.574 (6). Bond angles (deg): N(1)–Zr–N(2), 86.1 (2); Zr–N(2)–C(15) 91.4 (3); N(2)–C(15)–C(14), 121.7 (5); N(1)–C(14)–C(15) 124.5 (5); Zr–N(1)–C(14) 91.9 (3); cp(1)–Zr–Cp(2), 122.9 (2).

The molecular structure and numbering scheme are shown in Figure 1. For the sake of clarity the zirconium-containing ring will be referred to as ring A, while the adjoining organic heterocycle is denoted as ring B. The interatomic distances in ring A are consistent with substantial π-delocalization in the N–C–C–N system [C14–C15, 1.386 (9) Å; N1–C14, 1.380 (8) Å; N2–C15, 1.414 (7) Å]. In addition, the two Zr–N distances [2.150 (5) Å, Zr–N1; 2.116 (5) Å, Zr–N2] suggest significant d_π–p_π interaction between the ligand system and the metal, as they both are shorter than comparable Zr–N(σ) lengths, such as those found in $cp_2Zr(Cl)(C_6H_{11}NCH{=}NC_6H_{11})$ [average length 2.28 Å].[7a] Notably, these bond lengths are also

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(3) (a) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1984**, *23*, 1739–1747. (b) Robbins, J. L.; Edelstein, N.; Spencer, B.; Smart, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 1882–1893. (c) Treichel, P. M.; Johnson, J. W.; Wagner, K. P. *J. Organomet. Chem.* **1975**, *88*, 227–230.

(4) Jones, S. B.; Petersen, J. L. *Inorg. Chem.* **1981**, *20*, 2889–2894.

(5) Reaction details. All reactions were carried out under an atmosphere of purified nitrogen. **2a**: $[cp'_2ZrH(\mu\text{-}H)]_2$ (1.518 g, 89% pure, 2.04 mmol) was suspended in 50 mL of distilled THF. Distilled $(CH_3)_3CNC$ (25 mL, 22.10 mmol) was added by pipette. The solution turned yellow immediately, and with swirling it became orange-red as the starting material dissolved. After the solution was allowed to sit for 24 h at room temperature, the solvent was evaporated until approximately 1 mL remained. Distilled hexane (10 mL) was then added by pipette forming a clear orange solution. The solution was stored at room temperature. The product (1.535 g) was collected representing a 49% yield. **2b**: $[cp'_2ZrH(\mu\text{-}H)]_2$ (3.415 g, 88% pure, 6.0 mmol) was placed in 50 mL of distilled THF. Distilled $(C_6H_{11})NC$ (3.3 mL, 26.9 mmol) was added by pipette with stirring. The solution was monitored by IR and stored overnight at room temperature. Isocyanide (0.56 mL, 4.6 mmol) was then added, and the solution was again monitored by IR. A final addition of isocyanide (1.10 mL, 9.13 mmol) was followed by monitoring. The solution was stored at room temperature overnight. It was then evaporated to a few milliliters in volume, and 70 mL of distilled hexane was added. The solution was stored at −20 °C for 1 day and filtered to remove minor precipitation. The solution was then stored at −20 °C for 48 h and then moved to dry ice storage. After 24 h in dry ice storage, the solution was concentrated to two-thirds volume and restored in dry ice. After 5 days in dry ice a dark brown solid coated the flask. The solid was extracted into hexane and stored at room temperature. After 24 h it was filtered and again stored at room temperature for 24 h. The solution was then stored at −20 °C. After 5 days the crystalline product was filtered from solution.

(6) A crystal of **2a**, having the dimensions of 0.37 × 0.39 × 0.50 mm, was mounted on a Phillips PW 1100 diffractometer, equipped with a graphite monochromator. With Mo Kα (λ = 0.7107 Å) crystal data were as follows: triclinic, space group $P\bar{1}$; a = 10.371 (2) Å, b = 16.469 (3) Å, c = 9.330 (2) Å; α = 97.37 (1)°, β = 103.81 (1)°, γ = 81.52 (1)°; V = 1523.4 (5) Å^3; D_{calcd} = 1.273 g cm^{-3}; Z = 2. Data were collected to $2\theta_{max}$ = 47° with an $\omega/2\theta$ scan technique. A total of 4515 unique data were collected of which 2726 had $I > 3\sigma(I)$. The crystal quality was tested by ψ scans showing that crystal absorption affects could be neglected. The function minimized during the least-squares refinement was $w = k/\sigma^2(F_o) + |g|(F_o)^2|$. At the end of refinement the values for k and g were 1.0411 and 0.000 230. Scattering factors and corrections for anomalous scattering were from: International Tables; Knynoch Press: Birmingham, England, 1900; Vol. IV. Computer programs were those of SHELX-76 system. The structure was solved by the heavy-atom method starting from a three-dimensional Patterson map. Refinement was performed first isotropically and then anisotropically for non-H atoms, by full-matrix least-squares. Solution and refinement were based on the observed reflections [$I > 3\sigma(I)$]. Refinement was continued until no parameter shifted by more than 0.2 times its standard deviation. The R value was 0.047 (R_w = 0.046).

(7) (a) Gambarotta, S.; Strologo, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1985**, *107*, 6278–6182. (b) Van Bynum, R.; Hunter, W. E.; Rogers, R. D.; Atwood, J. L. *Inorg. Chem.* **1980**, *19*, 2368–2374. (c) Atwood, J. L.; Rogers, R. D.; Hunter, W. E.; Floriani, C.; Fachinetti, G.; Chiesi-Villa, A. *Inorg. Chem.* **1980**, *19*, 3812–3817. (d) Lappert, M. F.; Raston, C. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1984**, 893–902. (e) Kruger, C.; Müller, G.; Erker, G.; Dorf, U.; Engel, K. *Organometallics* **1985**, *4*, 215–223. (f) Erker, G.; Kruger, C.; Müller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1–38. (g) Hofmann, P.; Frede, M.; Stauffert, P.; Lasser, W.; Thewalt, U. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 712–713. (h) McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 1072–1073.

shorter than the Zr–N distances in $cp_2Zr-(\eta^1-NC_4H_4)_2$ [average bond length 2.169 (3) Å],[7b] the lengths of which were ascribed to $d_\pi-p_\pi$ metal–ligand interaction. Finally, the Zr–N bond lengths in **2a** are shorter than the Zr–C(carbonyl) bond length of 2.187 (4) Å, found in $cp_2Zr(CO)_2$,[7c] in which d orbital participation is expected due to the π-acid nature of the CO ligand.

Another manifestation of the same effect is reflected in the Zr–C14 [2.593 (5) Å] and Zr–C15 [2.574 (6) Å] bond lengths and in the position of the Zr atom 1.176 (1) Å below the N–C–C–N weighted least-squares plane. In a variety of zirconacycle analogues of **2a**, the C–C π density is observed to interact with the metal d orbitals. This σ^2,π-bonding arrangement has been found in Zr—C—C=C—C,[7d,e,f] Zr—O—C=C—O,[7g] and Zr—O—C=C—N[7h] systems; a limiting value for the Zr—C′ length (for the generalized structure Zr—C—C′=C′—C) of 2.855 (4) Å has been discussed.[7e] It has also been shown that the substituents on the C′ carbons play a role in the degree of zirconacycle folding;[7g] the steric congestion caused by bulkier substituents makes the σ^2,π structure less energetically accessible. An explanation of this sort may account for the N–C–C–N conformation in **2a**.

The bonding in ring B differs from that in ring A. All of the bond distances, with the exception of the C14–C15 double bond, correspond to single bond lengths. The exocyclic C16–N3 bond has a length of 1.259 (9) Å, consistent with a C–N double bond. Ring B, like ring A, is nonplanar and is puckered.

The Zr–cp lengths [2.294 (4) Å, Zr–cpl; 2.295 (4) Å, Zr–cp2] exceed the usual range of 2.23–2.26 Å. Likewise, the cpl(centroid)–Zr–cp2(centroid) angle, at 122.9 (2)°, is contracted; presumably, both effects are due to steric interaction between the *tert*-butyl groups and the cp rings.

That both **2a** and **2b** are analogous in structure is confirmed by mass spectrometry.[8] In each case, the parent peak is observed [**2a**, *m/e* 583; **2b**, *m/e* 687 (Zr − 91)] with correct isotopic ratios. Each mass spectrum displays a peak at $m^+ - 14$ which, in the case of **2a**, can only correspond to the loss of a CH_2 group; this peak presumably corresponds to the loss of the same group in **2b** (as opposed to the loss of a single CH_2 from one cyclohexyl group).

Proton NMR data are consistent with the structures proposed for the **2a** and **2b**. The methylene protons in both cases are nonequivalent. In **2a**, the methylene resonances appear as two doublets integrating to one proton each at δ 4.04 and 3.22.[9] In **2b**, the methylene peaks appear at δ 2.87 and 2.48.[10]

The mechanism of reaction 4 can only be a matter of speculation prior to further studies. However, there are literature precedents for several possible steps in the mechanism. The first step, after coordination of intact isocyanide, probably involves stepwise transfer of two hydrides to the carbon of the η^2-bonded RNC moiety, as in reaction 3.[2b] This is further confirmed by the presence of both hydrides on a single carbon in structures **2a** and **2b**. It should be noted that hydride transfers to isocyanides have been observed with a variety of metals.[11] Given the assumption of a stepwise hydride transfer, clearly two isocyanide molecules must insert into the Zr–N bond and one must insert into the Zr–C bond in order to obtain the observed structure. Isocyanide insertion into Zr–C(alkyl) bonds has been observed in a variety of cases.[2a,b,12a,b] The insertion of two RNC moieties into the M–N bond, of course, is actually two separate steps, only one of which is precedented. The unprecedented insertion is that of an isocyanide into the M—N bond to form an M—C(=NR)—N structure. While it has been reported that isocyanates insert preferentially into the M—N bond of a (η^2-ethyliminoethyl-*C,N*)tantalum complex,[13] no examples of C≡N– insertion into such M—N bonds exist in the literature. The second (precedented) insertion, that of an isocyanide group into a M—C(=NR) bond, has been observed with a variety of metals.[14-17] The order of these steps, of course (with the exception of the first), cannot be assigned without further investigation. Lastly, we note that, if the bicyclic ring forming step is the final step in the mechanism, then it may proceed through a dicarbene-like intermediate, similar to that invoked for the reaction of $cp_2Zr(CH_3)_2$ with CO.[18]

Finally, the role of the methyl substituent on cyclopentadiene remains unclear in view of the apparent difference in stoichiometry between reaction 4 and reactions 1–3. While it is possible that the greater metal-to-ligand donation of methylcyclopentadiene over unsubstituted cyclopentadiene plays a role in stabilizing the metal center during reaction and so facilitates the observed coupling, it is impossible to separate the ligand effect from that of the difference in stoichiometry. This question is under investigation. Lastly, we note that the dimeric **1** contains both bridging and terminal hydrides; the monomeric $(C_5Me_5)ZrH_2$ used in reactions 2 and 3 contains only terminal hydrides. The effect of this difference on the reactivity of the metal complexes with isocyanides also remains unclear and is under investigation.

Acknowledgment. We thank the National Science Foundation (Columbia University, Grant CHE-8512660) and Italian CNR (University of Parma) for financial support. We wish to thank Dr. Christopher Turner for his assistance with the NMR studies.

Registry No. 1, 77965-67-4; **2a**, 104465-54-5; **2b**, 104487-50-5; $(CH_3)_3CNC$, 7188-38-7; $(C_6H_{11})NC$, 931-53-3.

Supplementary Material Available: X-ray crystallography and references, crystallographic parameters (Table I), fractional

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[8] Acceptable analytical data were obtained for **2a**. Anal. Calcd: C, 65.81; H, 8.98; N, 9.59. Found: C, 65.34; H, 8.83; N, 9.51.

[9] Coupling was verified by a proton-decoupling experiment using $CDCl_3$ as solvent; J_{H-H} = 15 Hz. Other peaks are assigned as follows (cp rings arbitrarily lettered A and B). Rotation of the cp rings with respect to the NMR time scale is slow at room temperature; hence each proton displays a discrete resonance. NMR (300 MHz, δ): 6.21, 6.13, 5.90, 5.82 (doublet of triplets, 1 H, protons on cp ring A); 5.70, 4.90 (doublet of triplets, 1 H, protons on cp ring B); 5.30 (m, two overlapping doublets of triplets, 2 H, protons on cp ring B); 2.31, 2.21 (s, 3 H, methyl protons on cp ring); 1.56, 1.41, 1.34, 1.27 (s, 9 H, *tert*-butyl protons).

[10] Couplings were determined by a 2-D correlated spectroscopy experiment (COSY) using $CDCl_3$ as solvent (J_{H-H} = 6 Hz). Other peaks are assigned as follows (cp rings arbitrarily lettered): δ 6.14 (m, 1 H, cp ring A proton); 6.09 (m, 1 H, cp ring A proton); 5.79–5.84 (m, 2 H, cp ring A protons); 5.16 (doublet of triplets, 1 H, cp ring B proton); 5.04 (doublet of triplets, 1 H, cp ring B proton); 4.67 (d, 1 H, cp ring B proton); 4.62 (d, 1 H, cp ring B proton); 2.25, 2.00 (s, 3 H, methyl protons on cp rings); 1.1–2.2, 3.5, 3.7 (b, m, 44 H, cyclohexyl resonances).

[11] Christian, D. F.; Clarke, G. R.; Roper, N. R.; Waters, J. M.; Whittle, K. R. *J. Chem. Soc., Chem. Commun.* **1972**, 458–459. (b) Adams, D. R.; Golembeski, N. M. *J. Am. Chem. Soc.* **1979**, *101*, 2579–2587. (c) Christian, D. F.; Roper, W. R. *J. Organomet. Chem.* **1971**, *80*, C35–C38. (d) Clark, G. R.; Waters, J. M.; Whittles, K. R. *J. Chem. Soc., Dalton Trans.* **1975**, 2556–2560. (e) Christian, D. F.; Clark, H. C.; Stepaniak, R. F. *J. Organomet. Chem.* **1976**, *112*, 209–225.

[12] (a) Lappert, M. F.; Luong-Thi, N. T.; Milne, C. R. C. *J. Organomet. Chem.* **1979**, *174*, C35–C37. (b) Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organo-Zirconium and -Hafnium Compounds*; Ellis Horwood Limited: Chichester, 1986; pp 221–223.

[13] Takahashi, Y.; Onoyama, N.; Ishikawa, Y.; Motojima, S.; Sugiyama, K. *Chem. Lett.* **1978**, 525–528.

[14] Otsuka, S.; Nakamura, A.; Yoshida, T. *J. Am. Chem. Soc.* **1969**, *91*, 7196–7198.

[15] Yamamoto, Y.; Yamazaki, H. *Inorg. Chem.* **1972**, *11*, 211–214.

[16] Yamamoto, Y.; Yamazaki, H. *Inorg. Chem.* **1974**, *13*, 438–443.

[17] Yamamoto, Y.; Yamazaki, H. *Coord. Chem. Rev.* **1972**, *8*, 225–239.

[18] Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716–2724.

atomic coordinates (Table II), bond distances and angles (Table III), anisotropic thermal parameters (Table IV), and fractional atomic coordinates for H atoms (Table V) (9 pages); a listing of structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

Three-Fragment Oxidative Addition of Dichloromethane to a Mononuclear Rhodium(I) Complex with Concomitant Formation of a Metal–Phosphoranide Bond

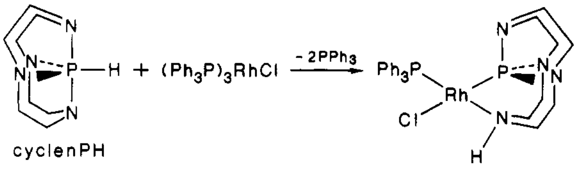
Elizabeth G. Burns,[†] **Shirley S. C. Chu,**[‡]
Patrice de Meester,[‡] **and Michael Lattman***[†]
Departments of Chemistry and Engineering
Southern Methodist University, Dallas, Texas 75275

Received July 22, 1986

Summary: Cyclenphosphorane reacts with $ClRh(PPh_3)_3$ to initially yield a four-coordinate complex where two PPh_3 groups have been displaced by the phosphorus and one nitrogen atom of the open form of cyclenphosphorane. This species undergoes a three-fragment oxidative addition of dichloromethane to yield a compound with a phosphoranide–metal bond and a novel P–N–C–Rh metallacycle.

Oxidative addition of dihalomethanes to low-valent transition metals is well-documented.[1] In general, these reactions lead to halomethyl[1a–f] (CH_2X-M-X, CH_2X-M^+X^-) and methylene-bridged[1g–j] (X-M-CH_2-M-X) derivatives.[2] We herein report the synthesis of a new Rh(I) species which undergoes a three-fragment oxidative addition of CH_2Cl_2. The addition is accompanied by an intramolecular ligand rearrangement to yield a covalent phosphoranide–rhodium(III) complex (R_4P–Rh) with a P–N–C–Rh four-membered ring. To our knowledge, this is the first reported example of a three-fragment oxidative addition of CH_2X_2 to a single metal center, as well as the first rhodium complex with a phosphoranide ($R_4P{:}^-$) ligand.

Wilkinson's catalyst reacts with cyclenphosphorane (cyclenPH)[3] according to eq 1. Compound 1 was synthesized by treating 1.12 g (1.21 mmol) of $ClRh(PPh_3)_3$ with 0.243 g (1.21 mmol) of cyclenPH at −50 °C in THF. The stirred mixture was allowed to warm to ambient temperature over 1 h and stirring continued for another 3 h. After filtration, the precipitated solid was washed with THF and pumped dry to yield 0.570 g of 1[4] (78%) as a highly oxygen-sensitive yellow solid. The $^{31}P\{^1H\}$ NMR spectrum of 1 (CD_2Cl_2) shows an ABX pattern with δ 157 (dd, PN, $^1J_{RhP}$ = 227 Hz), 53 (dd, PC, $^1J_{RhP}$ = 198 Hz), and $^2J_{PP}$ = 52 Hz. The large downfield shift of the nitrogen-bound phosphorus compared to cyclenPH (δ −55) is indicative of P–N bond cleavage. Similar reactivity and chemical shifts have been reported for the related molecule cyclamPH with other transition-metal compounds.[5] The cis arrangement of phosphorus atoms is suggested by the relatively small $^2J_{PP}$ value,[6] and the presence of the N–H bond is confirmed by the observation of a broad, low-in-



cyclenPH

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(1)

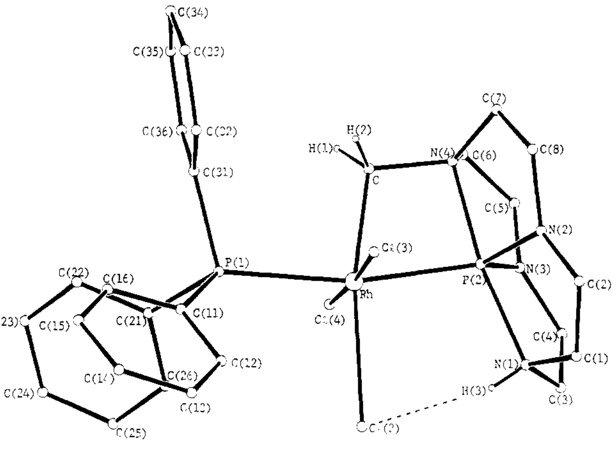

Figure 1. Geometry of the Rh(III) complex 2. Atoms are represented as circles of arbitrary radii. All H atoms excluded for clarity except H(1) and H(2) belonging to the bridging CH_2 group and H(3) involved in an intramolecular H bond.

Table I. Selected Bond Distances (Å) and Angles (deg) for 2

	Bond Distances		
Rh–P(1)	2.407 (2)	C–N(4)	1.49 (1)
Rh–Cl(2)	2.549 (2)	P(2)–N(1)	1.931 (7)
Rh–Cl(3)	3.354 (2)	P(2)–N(2)	1.661 (6)
Rh–Cl(4)	2.351 (2)	P(2)–N(3)	1.677 (7)
Rh–P(2)	2.271 (2)	P(2)–N(4)	1.911 (8)
Rh–C	2.032 (6)		
	Bond Angles		
P(1)–Rh–P(2)	168.6 (1)	Rh–P(2)–N(4)	83.8 (2)
Cl(2)–Rh–C	169.6 (2)	P(2)–Rh–C	73.6 (2)
Cl(3)–Rh–Cl(4)	176.7 (1)	N(1)–P(2)–N(4)	170.6 (3)
Rh–C–N(4)	104.4 (4)	N(2)–P(2)–N(3)	112.4 (3)
P(2)–N(4)–C	98.0 (5)		
	H Bond Geometry		
N(1)···Cl(2)	3.138 (7)	N(1)–H(3)–Cl(2)	163 (5)°
H(3)···Cl(2)	2.40 (5)		

[†] Department of Chemistry.

[‡] Department of Engineering.

(1) See, for example: (a) Kermode, N. J.; Lappert, M. F.; Skelton, B. W.; White, A. H.; Holton, J. *J. Chem. Soc., Chem. Commun.* **1981**, 698. (b) Scherer, O. J.; Jungman, H. *J. Organomet. Chem.* **1981**, *208*, 153. (c) Collman, J. P.; Murphy, D. W.; Dolcetti, G. *J. Am. Chem. Soc.* **1973**, *95*, 2687. (d) Werner, H.; Paul, W. *J. Organomet. Chem.* **1982**, *236*, C71. (e) Olson, W. L.; Nagaki, D. A.; Dahl, L. F. *Organometallics* **1986**, *5*, 630. (f) Labinger, J. A.; Osborn, J. A.; Coville, N. J. *Inorg. Chem.* **1980**, *19*, 3236. (g) Murray, H. H.; Fackler, J. P.; Mazany, A. M. *Organometallics* **1984**, *3*, 1310. (h) Amane, M. E.; Maisonnat, A.; Dahan, F.; Pince, R.; Poilblanc, R. *Organometallics* **1985**, *4*, 773. (i) Jandik, P.; Schubert, U.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 73. (j) Balch, A. L.; Hunt, C. T.; Lee, C.-L.; Olmstead, M. M.; Farr, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 3764.

(2) Other products have also been observed: (a) Werner, H.; Zolk, R. *Organometallics* **1985**, *4*, 601 (sulfur–metal bridge insertion of CH_2). (b) Scherer, O. J.; Jungman, H.; Hussong, K. *J. Organomet. Chem.* **1983**, *247*, C1 (formation of a carbonato ligand). (c) Klein, H.-F.; Hammer, R. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 42. (d) Werner, H.; Hofman, L.; Paul, W. *J. Organomet. Chem.* **1982**, *236*, C65. (e) Kermode, N. J.; Lappert, M. F.; Skelton, B. W.; White, A. H.; Holton, S. *J. Organomet. Chem.* **1982**, *228*, C71 (formation of metallo-bonded phosphorus ylides).

(3) (a) Richman, J. E.; Atkins, T. J. *Tetrahedron Lett.* **1978**, 4333. (b) Atkins, T. J.; Richman, J. E. *Tetrahedron Lett.* **1978**, 5149.

(4) Anal. Calcd for $C_{26}H_{32}ClN_4P_2Rh$: C, 51.96; H, 5.38; N, 9.33; Cl, 5.90. Found: C, 50.90; H, 5.34; N, 9.16; Cl, 6.05. ^1H NMR data (200 MHz, CD_2Cl_2): δ 2.3–3.0 (comp m, CH_2, 16 H), 5.1 (br, NH, 1 H), 7.31, 7.68 (m, CH, 15 H).

(5) The molecule cyclamPH has alternating $(CH_2)_2$ and $(CH_2)_3$ groups bridging the nitrogen atoms. (a) Dupart, J.-M.; Grand, A.; Riess, J. G. *J. Am. Chem. Soc.* **1986**, *108*, 1167. (b) Dupart, J.-M; Grand, A.; Pace, S.; Riess, J. G. *J. Am. Chem. Soc.* **1982**, *104*, 2316.

(6) (a) Verkade, J. G. *Coord. Chem. Rev.* **1972/1973**, *9*, 1. (b) Pregosin, P. S.; Kunz, R. W. "^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes" In *NMR, Basic Principles and Progress*; Diehl, P., Flack, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin, 1979.

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