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SYNTHESIS OF Zr–Re-CONTAINING POLYHYDRIDES BY AMINE ELIMINATION

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Summary

The reaction between $Zr(C_5H_5)_2(X)(NMe_2)$ and $ReH_7(PPh_3)_2$ results in the production of the heterometallic polyhydrides $(C_5H_5)_2Zr(X)[H_6Re(PPh_3)_2]$ [(I), X = Cl; (II), $X = NMe_2$] with the elimination of $HNMe_2$. Both compounds were characterized spectroscopically and the structure of (I) was determined by X-ray diffraction. Compound (I) crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 12.011(4)$ Å, $b = 10.151(3)$ Å, $c = 33.23(1)$ Å and $V = 4051.74$ Å^3. Full-matrix least squares refinement converged at $R = 6.55\%$ and $R_w = 6.14\%$. $ReH_7(PPh_3)_2$ also reacts with $Zr(NMe_2)_4$ in a 1:1 or 2:1 mole ratio to produce $(NMe_2)_3Zr[H_6Re(PPh_3)_2]$ (III) and $(NMe_2)_2Zr[H_6Re(PPh_3)_2]_2$ (IV) with the elimination of one or two equivalents of $HNMe_2$, respectively. The structure of (IV) was determined by X-ray diffraction. Compound (IV) crystallizes in the monoclinic space group $P2_1/n$ with $a = 13.550(6)$ Å, $b = 34.13(2)$ Å, $c = 14.735(6)$ Å, $\beta = 90.71(2)°$ and $V = 6813.19$ Å^3. Full-matrix least-squares refinement converged at $R = 10.4\%$ and $R_w = 9.3\%$. The reactivity of these compounds with simple substrates such as CO and CO_2 has been surveyed and compared with that of the previously known Zr–Re polyhydride $(C_5H_5)_2Zr(H)[H_6Re(PMePh_2)_2]$.

Introduction

Compounds containing both early and late transition metals have become a topic of current interest due to their potential to activate synthesis gas mixtures, composed of CO and H_2. This potential is based on the hypothesis that two electronically-different transition metals in close proximity may cooperate in the reduction of dipolar substrates (*e.g.*, CO, CO_2). In addition to reactions typical of mononuclear transition metal compounds, such as oxidative addition, reductive elimination, substitution and migratory

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insertion into metal–ligand bonds, the presence of a metal–metal bond in such compounds introduces the possibility of additional reactivity due to cleavage of, or insertion into, the metal–metal bond. One reason early-to-late transition metal compounds have failed to react with such substrates is the difficulty with which hydrogen is introduced into these compounds. A solution to this problem is to couple metal complexes already incorporating hydride ligands, to assure their presence in the final product.

The best-established method of synthesizing a hetero-transition metal compound is the reaction between a transition metal halide and an anionic transition metal complex [1]. The first documented example of a compound with an early-to-late transition metal bond was made in such a manner [2]. Casey and coworkers have made a series of compounds with Zr—Ru or Zr—Fe bonds using this method [3]. This type of reaction has subsequently been used to make compounds with U—Fe, U—Ru, Th—Fe and Th—Ru bonds [4]. Several Zr–Os or Zr–Re polyhydride compounds have also been made in this way [5].

Another approach to the formation of metal–metal bonds is the bimolecular reductive elimination reaction [1]. This procedure has the advantage of avoiding possible redox complications which can occur in metal halide/metalate reactions. In addition, it obviates the necessity of halide-containing starting materials which may not be accessible synthetically. Warner and Norton have utilized this approach successfully, reacting alkyl transition metal carbonyls with transition metal hydrides to form a bimetallic compound with the production of an aldehyde [6]. Bercaw and coworkers have used bimolecular dihydrogen elimination reactions to produce compounds with Zr—Ru, Zr—Co and Zr—Rh bonds [7]. The group of Boersma has reported elimination of cyclopentadiene between transition metal hydrides and $(C_5H_5)_2Zn$ [8]. Methane elimination reactions between ReH_7P_2 or ReH_5P_3 and Al_2Me_6 results in Re–Al compounds [9].

The amine elimination reaction between a transition metal amide, $M—NR_2$, and a transition metal hydride, $M'—H$, has proven to be a particularly versatile method for the formation of hetero-transition metal compounds. Reactions of $[Me(CH_2PR_2)_3]MH_3$ (M = Rh, Ir; R = Me, Ph) with ZnX_2 ($X = N(SiMe_3)_2$, $OC_6H_2(CMe_3)_3$) result in Zn–M compounds, with the elimination of $HN(SiMe_3)_2$ or $C_6H_2(CMe_3)_3OH$ [10]. The reaction between $Ti(NMe_2)_4$ and $MH(CO)_2(C_5H_5)$ (M = Fe, Ru) results in the formation of a Ti—M bond with the production of $HNMe_2$ [11]. Recently, this method has been extended to compounds bearing a mixed amido/alkoxy ligand set on titanium [12].

Here we report the extension of dimethylamine elimination to the production of polyhydride compounds containing Zr and Re. Dimethylamine elimination is particularly favored due to the volatility of the amine, which serves to drive the reaction to completion. Moreover, no compound currently exists linking two different metal elements by an M=M′ double bond. The amine elimination method, if carried out between a polyhydride and a diamide, is therefore explored as a route to such a compound [eqn. (1)].

$$L_nM(NMe_2)_2 + L_mM'H_x \rightarrow L_nM{=}M'H_{x-2}L_m + 2NHMe_2 \quad (1)$$

We also report our efforts to survey the reactivity of these compounds with CO and CO_2, and compare this reactivity to that of previously-reported [5] $(C_5H_5)_2Zr(H)[H_6Re(PMePh_2)_2]$ and $(C_5H_5)_2ZrH[H_3Os(PMe_2Ph)_3]$.

Experimental

All manipulations were carried out under a dry, oxygen-free nitrogen atmosphere, either via standard Schlenk techniques or in a Vacuum Atmospheres glove box. All solvents were distilled under nitrogen from sodium benzophenone ketyl and stored under nitrogen until use. $Zr(C_5H_5)_2(NMe_2)_2$ [13], $Zr(NMe_2)_4$ [14] and $ReH_7(PPh_3)_2$ [15] were all made using literature methods. CO was supplied by Matheson and used as received. CO_2 ('anerobe purity') was supplied by Matheson and dried over activated molecular sieves for at least one week before use.

NMR spectra were obtained on a Nicolet NT-360 spectrometer using C_6D_6 solutions and are reported in δ units. ^1H NMR spectra were recorded at 360 MHz with C_6D_5H as an internal reference. ^{31}P NMR spectra were ^1H decoupled and were recorded at 146.19 MHz, referenced to 85% H_3PO_4 solution. Crystals for X-ray diffraction studies were handled as described previously [16].

Syntheses

$(C_5H_5)_2Zr(NMe_2)Cl$

$(C_5H_5)_2Zr(NMe_2)Cl$ was prepared in a similar manner to $(C_5H_5)_2Zr(NMe_2)_2$ [13]. Thus 4.999 g (17.11 nmol) Cp_2ZrCl_2 was stirred in 125 ml THF at 0 °C. Then $LiNMe_2$ (0.876 g, 17.2 mmol) was added slowly via a solids addition tube, causing the mixture to become yellow. After the addition was complete, the mixture was allowed to stir at 25 °C for 17 h. Volatiles were then removed *in vacuo* to yield a yellow solid. Sublimation (*ca.* 100 °C, 0.06 Torr) afforded the product as a yellow solid. Yield: 1.49 g, 29.0%. ^1H NMR spectroscopy: 5.84 (C_5H_5); 2.83 (NMe_2).

$(C_5H_5)_2Zr(Cl)[H_6Re(PPh_3)_2]$ (I)

$(C_5H_5)_2Zr(NMe_2)Cl$ (200 mg, 0.665 mmol) and 476 mg (0.664 mmol) $ReH_7(PPh_3)_2$ were dissolved in 60 ml toluene and stirred at 25 °C for 5 h. Toluene was then removed *in vacuo* until the solution volume was *ca.* 5 ml and a yellow solid had begun to precipitate. Pentane (15 ml) was added dropwise to complete the precipitation of the product, which was isolated by filtration, rinsed with 5 ml pentane and dried under vacuum. Yield: 510 mg, 80%. ^1H NMR spectroscopy: 7.64, 6.98 (m, C_6H_5); 6.01 (s, C_5H_5); -3.42 (t, $J = 14$ Hz, Re—H). ^{31}P NMR spectroscopy: 33.1 (s, PPh_3).

$(C_5H_5)_2Zr(NMe_2)[H_6Re(PPh_3)_2]$ (II)

$ReH_7(PPh_3)_2$ (154 mg, 0.215 mmol) and 66 mg (0.22 mmol)$(C_5H_5)_2Zr(NMe_2)_2$ were dissolved in 20 ml toluene and stirred at room temperature for 15 h. The resulting clear yellow solution was evaporated to dryness to give a yellow–orange residue. The residue was redissolved in a 4 ml toluene and slow addition of 4 ml heptane caused the product to precipitate as a yellow powder, which was isolated by filtration (yield: 36 mg). The filtrate was evaporated to a yellow residue which was triturated with 5 ml heptane. Filtration of the resulting suspension afforded an additional 25 mg product. Total yield: 61 mg, 28%. ^{1}H NMR spectroscopy: 7.68, 6.96 (m, C_6H_5); 5.92 (s, C_5H_5); 2.70 (s, NMe_2); −5.01 (t, $J = 15$ Hz, Re—H). ^{31}P NMR spectroscopy: 37.0 (s).

$(NMe_2)_3Zr[H_6Re(PPh_3)_2]$ (III)

$Zr(NMe_2)_4$ (114 mg, 0.427 mmol) and 304 mg (0.423 mmol) $ReH_7(PPh_3)_2$ were stirred in 30 ml pentane at room temperature for 14 h, during which time the product precipitated. The volume of the solution was then reduced by 50% under vacuum. Filtration and drying of the resulting solid afforded the product as a white solid. Yield: 261 mg, 66%. ^{1}H NMR spectroscopy: 7.63, 6.92 (m, C_6H_5); 3.07 (s, NMe_2); −4.84 (t, $J = 13$ Hz, Re—H). ^{31}P NMR spectroscopy: 32.7 (s).

$(NMe_2)_2Zr[H_6Re(PPh_3)_2]_2$ (IV)

$ReH_7(PPh_3)_2$ (300 mg, 0.418 mmol) and 56 mg (0.21 mmol $Zr(NMe_2)_4$ were dissolved in 20 ml benzene and stirred at room temperature for 16 h. Volatiles were removed *in vacuo* to yield a yellow–orange sticky residue. Trituration with 5 ml pentane afforded the product as a yellow powder, which was isolated by filtration and dried. Yield: 253 mg, 75%. ^{1}H NMR spectroscopy: 7.66, 6.90 (m, C_6H_5); 3.07 (s, NMe_2); −3.89 (t, $J = 13$ Hz, Re—H). ^{31}P NMR spectroscopy: 31.7 (s).

Reaction of compounds with gaseous substrates

General procedure

A sample of the compound (*ca.* 20 mg) was dissolved in 0.5 ml C_6D_6 in an NMR tube. The solution was degassed by two freeze–pump–thaw cycles. The sample was then frozen, evacuated and placed under the gaseous substrate at 1 atm pressure, then allowed to warm to room temperature and sealed. Any reaction which occurred was monitored by NMR spectroscopy.

$(C_5H_5)_2Zr(H)[H_6Re(PMePh_2)_2]$ with CO_2

In a 100 ml Schlenk flask, 1 atm of carbon dioxide was added to a degassed solution of $(C_5H_5)_2Zr(H)[H_6Re(PMePh_2)_2]$ (0.10 g) in benzene. After 1 h stirring at room temperature, the yellow solution had turned a light red color. The product was identified as $(C_5H_5)_2Zr(O_2CH)[H_6Re(PMePh_2)_2]$. $^{31}P\{^1H\}$ (C_6H_6) spectroscopy: 8.63 (s). ^{1}H NMR(C_6D_6) spectroscopy: 8.59 (HCO_2, s, 1H), 7.62, 7.01 (PPh, m), 6.19 (C_5H_5, s, 10H), 1.89 (PMe, d, $J = 7.5$ Hz, 6H), −4.14 (Re—H, t, $J = 15$ Hz, 6H). IR spectroscopy: 1640 cm^{-1} (O—C—O, str.), as a Fluorolube mull.

$(C_5H_5)_2Zr(H)[H_3Os(PMe_2Ph)_3]$ with CO_2

A THF solution of $(C_5H_5)_2Zr(H)[H_3Os(PMe_2Ph)_3]$ (0.05 g, 0.06 mmol) was degassed and then pressurized with excess CO_2 and stirred for 2 h. Solvent and excess CO_2 were removed under vacuum, leaving a yellow powder. ^1H NMR (C_6D_6, 25 °C) spectroscopy: −7.60 (second-order multiplet, 3H), 1.45 (d, J(Me—P) = 7 Hz, 18H), 6.14 (s, 10H), 7.0 - 8.0 (m, P—Ph), 8.73 (s, HCO_2). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C) spectroscopy: −27.3 (s). IR spectroscopy: 1642 cm^{-1} (O_2CH str.), as a Fluorolube mull.

Crystallographic studies

$(C_5H_5)_2Zr(Cl)[H_6Re(PPh_3)_2]$

A suitable crystal, grown by layering pentane onto a toluene solution of (**I**), was located and transferred to the goniostat using standard inert-atmosphere handling techniques and cooled to −155 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences corresponding to an orthorhombic space group with axial extinctions of $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; and $00l$, $l = 2n + 1$, corresponding to $P2_12_12_1$. Subsequent solution and refinement of the structure confirmed this choice. Parameters of the crystal, data collection and refinement are shown in Table 1. Data were collected in the usual manner [16] using a continuous

TABLE 1

Crystal data for $(C_5H_5)_2ZrCl\{H_6Re(PPh_3)_3\}$ and $(Me_2N)_2Zr\{H_6Re(PPh_3)_2\}_3$

formula	$C_{46}H_{44}P_2ClReZr$	$C_{76}H_{84}N_2P_4Re_2Zr$
color	orange	yellow
crystal dimensions (mm)	0.12 × 0.12 × 0.18	0.04 × 0.04 × 0.12
space group	$P2_12_12_1$	$P2_1/n$
cell dimensions	(at −155°C)	(at −150 °C)
a =	12.011(4) Å	13.550(6) Å
b =	10.151(3)	34.126(18)
c =	33.232(13)	14.735(6)
β =	90.0°	90.71(2)°
molecules/cell	4	4
volume (Å^3)	4051.74	6813.19
calculated density (g cm^{-3})	1.593	1.573
wavelength (Å)	0.71069	0.71069
molecular weight	971.67	1613.03
linear absorption coefficient (cm^{-1})	34.5	38.8
number of unique intensities	3017	8868
number with $F > 0.0$		6962
number with $F > 2.33\sigma(F)$	2364	4155
final residuals		
$R(F)$ =	0.0655	0.1036
$R_w(F)$ =	0.0614	0.0933
goodness of fit for the last cycle	0.93	1.46
maximum Δ/σ for last cycle	0.05	1.28

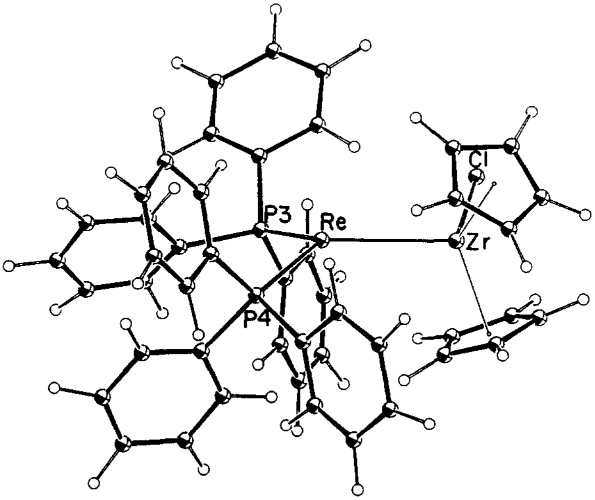

Fig. 1. ORTEP drawing of $(C_5H_5)_2ZrCl\{H_6Re(PPh_3)_2\}$, showing selected atom labeling. Hydride atoms were not located. Open circles are hydrogen; other unlabeled atoms are carbon.

θ–2θ scan ($6° \leqslant 2\theta \leqslant 45°$) with fixed backgrounds. Data were reduced to a unique set of intensities and associated sigmas in the usual manner. Averaging for the 738 reflections measured more than once gave $R = 0.038$. The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques. The absolute configuration for the crystal examined was determined by refinement using the two possible chiralities. Because of the low data-to-parameter ratio, carbon atoms were refined isotropically, and only the metal, chlorine and phosphorus atoms were refined anisotropically. Several of the hydrogen atoms were visible in a difference Fourier phased on the nonhydrogen atoms, and idealized positions were used for all carbon-bound hydrogens for the final cycles. It was not possible to detect the hydrides in the final difference Fourier (numerous peaks up to 1.3 e Å^{-3} were present in the vicinity of the metals). The results of the structure determination are shown in Tables 2 and 3 and in Figs. 1 and 2.

$(Me_2N)_2Zr[H_6Re(PPh_3)_2]_2$

A crystal, grown by layering pentane onto a benzene solution of the compound, was mounted using silicone grease and transferred to a goniostat where it was cooled to *ca.* −150 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space revealed Laue symmetry and systematic absences which determined the space group to be $P2_1/n$. During data collection ($6° \leqslant 2\theta \leqslant 45°$), four standards measured every 300 data showed no significant trends. After absorption correction, the residual for the averaging of redundant data was 0.056 for 1598 unique data

TABLE 2

Fractional coordinates[a] and isotropic thermal parameters[b] for $Cp_2ZrClH_6Re(PPh_3)_2$

	x	y	z	$10B_{iso}$
Re(1)	2550(1)	596(1)	1296.7(3)	12
Zr(2)	3568(2)	1867(3)	579(1)	14
P(3)	614(5)	198(6)	1376(2)	12
P(4)	3373(6)	−1102(7)	1702(2)	16
C(5)	5140(26)	2678(31)	1016(10)	30(6)
C(6)	4299(22)	3629(26)	1040(8)	19(5)
C(7)	4349(23)	4224(30)	669(8)	25(6)
C(8)	5037(24)	3521(28)	425(9)	21(6)
C(9)	5589(26)	2606(30)	642(9)	30(6)
C(10)	2849(27)	−29(32)	156(10)	38(7)
C(11)	3751(27)	−460(37)	310(10)	38(7)
C(12)	4661(25)	248(30)	172(9)	29(6)
C(13)	4249(25)	1179(29)	−103(9)	26(6)
C(14)	3108(25)	951(29)	−128(9)	28(6)
C(15)	−81(21)	−505(29)	924(7)	17(5)
C(16)	−881(21)	161(25)	704(8)	17(5)
C(17)	−1354(23)	−478(31)	368(8)	26(5)
C(18)	−997(22)	−1648(27)	250(8)	20(5)
C(19)	−261(26)	−2364(32)	457(10)	32(7)
C(20)	198(23)	−1839(29)	786(8)	22(5)
C(21)	164(20)	−926(24)	1783(7)	13(5)
C(22)	−622(24)	−1907(31)	1753(9)	26(6)
C(23)	−908(28)	−2640(34)	2061(10)	38(7)
C(24)	−484(23)	−2365(27)	2430(8)	20(5)
C(25)	275(23)	−1345(28)	2501(9)	20(6)
C(26)	616(21)	−656(29)	2168(7)	16(5)
C(27)	−307(22)	1606(27)	1462(8)	19(5)
C(28)	−82(22)	2772(26)	1215(8)	18(5)
C(29)	9194(22)	3861(26)	1227(8)	20(5)
C(30)	−1775(20)	3775(24)	1444(7)	12(5)
C(31)	−2060(20)	2626(25)	1677(8)	18(5)
C(32)	−1290(22)	1570(26)	1677(8)	22(5)
C(33)	3810(20)	9258(26)	2224(7)	12(5)
C(34)	3454(19)	358(22)	2432(6)	8(4)
C(35)	3763(19)	598(27)	2828(7)	14(4)
C(36)	4508(21)	−231(25)	3011(7)	16(5)
C(37)	4911(24)	−1322(28)	2804(9)	22(6)
C(38)	4576(23)	−1590(29)	2423(9)	21(6)
C(39)	4753(23)	−1540(28)	1492(8)	22(6)
C(40)	5632(23)	9371(32)	1513(8)	26(5)
C(41)	6603(22)	−861(26)	1316(9)	26(5)
C(42)	6812(23)	−2009(28)	1070(8)	24(5)
C(43)	5928(21)	−2953(27)	1047(8)	19(5)
C(44)	4936(18)	−2668(22)	1239(7)	9(4)
C(45)	2676(21)	−2717(21)	1754(7)	13(5)
C(46)	2550(29)	−3314(25)	2121(7)	24(5)
C(47)	2038(24)	−4561(33)	2146(9)	31(6)
C(48)	1780(22)	−5266(26)	1804(8)	22(5)
C(49)	1877(23)	−4608(29)	1420(8)	26(6)
C(50)	2393(24)	−3378(22)	1413(6)	16(5)
Cl(51)	1969(6)	3280(7)	357(2)	24

[a] Fractional coordinates are × 10^4.

[b] Isotropic values for those atoms refined anisotropically are calculated using the formula given by W. C. Hamilton, *Acta Crystallogr.*, *12* (1959) 609.

TABLE 3

Selected bond distances (Å) and angles (°) for $Cp_2ZrClH_6Re(PPh_3)_2$

(a) Distances			
Re(1)	Zr(2)	2.975(3)	
Re(1)	P(3)	2.374(6)	
Re(1)	P(4)	2.401(7)	
Zr(2)	Cl(51)	2.508(7)	
Zr(2)	C(5)	2.52(3)	
Zr(2)	C(6)	2.514(27)	
Zr(2)	C(7)	2.59(3)	
Zr(2)	C(8)	2.49(3)	
Zr(2)	C(9)	2.55(3)	
Zr(2)	C(10)	2.54(3)	
Zr(2)	C(11)	2.54(4)	
Zr(2)	C(12)	2.50(3)	
Zr(2)	C(13)	2.51(3)	
Zr(2)	C(14)	2.59(3)	
(b) Angles			
Zr(2)	Re(1)	P(3)	124.42(17)
Zr(2)	Re(1)	P(4)	126.30(18)
P(3)	Re(1)	P(4)	102.65(23)
Re(1)	Zr(2)	Cl(51)	99.71(18)

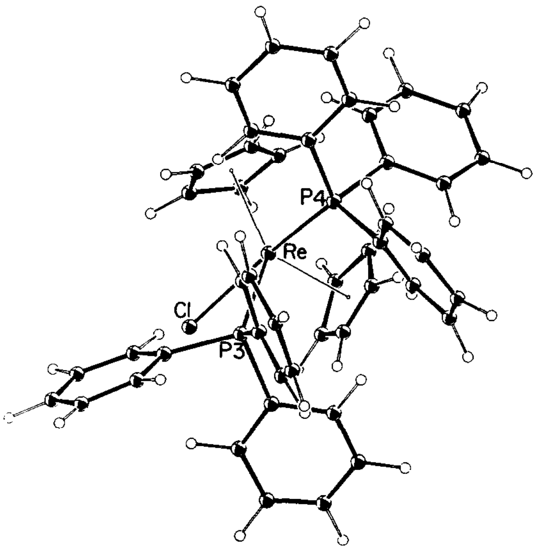

Fig. 2. ORTEP drawing of $Cp_2ZrCl\{H_6Re(PPh_3)_2\}$ viewed down the Zr–Re vector, showing the nonplanarity of the Zr ReP_2 unit, the staggered rotational conformation and the inequivalence of P3 and P4 in the ground state.

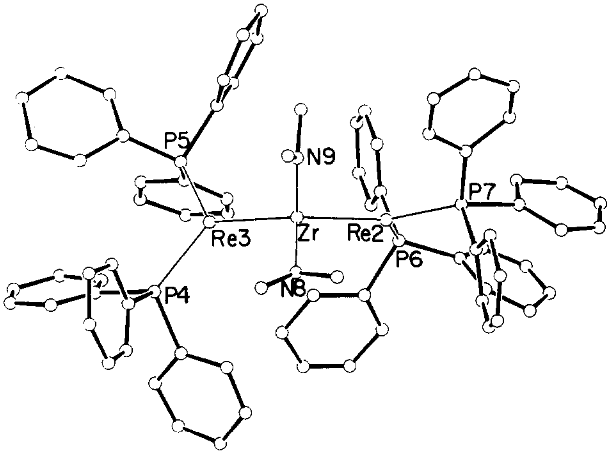

Fig. 3. ORTEP drawing of $(Me_2N)_2Zr\{H_6Re(PPh_3)_2\}_2$, showing selected atom labeling. Unlabeled atoms are carbon; hydrogen atoms have been omitted.

which were measured more than once. Parameters of the crystal and the data collection are shown in Table 1.

The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques. The data were quite weak and some of the carbon atoms, although clearly forming phenyl rings, did not refine well; methyl carbons on one of the $N(CH_3)_2$ groups were two-folded disordered and were modeled as four carbons with variable occupancies. No attempt was made to locate any hydrogens, although those attached to carbons were included in fixed calculated positions to improve the refinement of the nonhydrogen atoms. The final refinement used isotropic temperature factors on all carbon and nitrogen atoms.

The largest peak in the final difference map was 1.86 e Å^{-3}. The results of the structure determination are shown in Tables 4 and 5 and in Fig. 3, which shows only one pair of the disordered methyl groups on N8.

Results

$ReH_7(PPh_3)_2$ reacts with the compounds $(C_5H_5)_2Zr(X)(NMe_2)$ to produce the mixed-metal compounds $(C_5H_5)_2Zr(X)ReH_6(PPh_3)_2$ (X = Cl (**I**) and NMe_2 (**II**)) with concomitant elimination of $HNMe_2$. These compounds are yellow, air-sensitive solids which are soluble in common aromatic organic solvents and sparingly soluble in saturated hydrocarbons. The ^1H NMR signal of the hydride ligands in both compounds occurs as a triplet due to coupling to the two phosphines, implying that the hydrides are rapidly fluxional on the NMR timescale. Rapid hydride site exchange is apparent

TABLE 4

Fractional coordinates[a] and isotropic thermal parameters[b] for $(Me_2N)_2Zr[H_6Re(PPh_3)_2]_2$

	x	y	z	$10B_{iso}$
Zr(1)	7966(3)	9008(1)	4434(3)	15
Re(2)	6019(1)	8802(1)	4769(1)	12
Re(3)	8815(1)	8760(1)	2747(1)	16
P(4)	9305(8)	9236(3)	1615(9)	22
P(5)	9111(8)	8093(4)	2263(8)	20
P(6)	4813(8)	8540(4)	3703(8)	19
P(7)	5298(10)	8897(4)	6220(8)	24
N(8)	8127(26)	9600(10)	4524(24)	22(7)
N(9)	8872(23)	8840(10)	5522(21)	18(6)
C(10)	7826(54)	9819(22)	5413(50)	12(7)
C(11)	8872(56)	9824(24)	4349(55)	47(7)
C(12)	9504(43)	9041(18)	5997(40)	55(10)
C(13)	8919(46)	8421(19)	5719(42)	63(10)
C(14)	8259(35)	9557(14)	1134(32)	31(9)
C(15)	7602(37)	9741(15)	1725(33)	39(9)
C(16)	6881(43)	9990(18)	1410(40)	54(10)
C(17)	6801(47)	10056(19)	523(43)	64(10)
C(18)	7417(36)	9844(14)	−10(33)	34(9)
C(19)	8176(36)	9606(15)	224(33)	36(9)
C(20)	10295(40)	9609(16)	2002(37)	44(10)
C(21)	10179(37)	9992(16)	1755(34)	37(9)
C(22)	10790(37)	10264(15)	1955(33)	38(9)
C(23)	11613(34)	10123(14)	2396(30)	30(9)
C(24)	11856(49)	9746(20)	2709(45)	71(9)
C(25)	11083(34)	9471(14)	2467(31)	30(9)
C(26)	9910(34)	9073(14)	546(31)	32(9)
C(27)	10718(27)	9232(11)	183(25)	13(7)
C(28)	11098(35)	9076(14)	−587(32)	34(9)
C(29)	10629(26)	8753(13)	−1044(24)	15(7)
C(30)	9772(31)	8579(13)	−666(29)	26(8)
C(31)	9418(29)	8774(14)	153(26)	22(7)
C(32)	10284(26)	7942(10)	1935(24)	6(6)
C(33)	11042(32)	8204(13)	1535(29)	25(8)
C(34)	11930(30)	8094(13)	1155(28)	22(8)
C(35)	12154(34)	7678(14)	1176(31)	32(9)
C(36)	11489(31)	7421(13)	1555(28)	22(8)
C(37)	10540(36)	7554(14)	1864(33)	34(9)
C(38)	8311(34)	7931(14)	1402(31)	30(9)
C(39)	8667(29)	7784(12)	516(27)	17(7)
C(40)	8099(30)	7677(13)	−201(28)	23(8)
C(41)	7042(31)	7690(13)	−95(29)	22(8)
C(42)	6653(34)	7812(14)	717(32)	31(9)
C(43)	7235(35)	7941(14)	1397(32)	34(9)
C(44)	8914(28)	7727(11)	3157(26)	13(7)
C(45)	9388(36)	7754(15)	3946(34)	38(9)
C(46)	9395(37)	7468(15)	4576(34)	38(9)

TABLE 4 continued

Fractional coordinates[a] and isotropic thermal parameters[b] for $(Me_2N)_2Zr[H_6Re(PPh_3)_2]_2$

	x	y	z	$10B_{iso}$
C(47)	8783(26)	7089(11)	4409(24)	8(7)
C(48)	8285(38)	7091(16)	3663(35)	43(9)
C(49)	8344(36)	7371(15)	2975(33)	37(9)
C(50)	4767(25)	8784(13)	2564(23)	14(7)
C(51)	5633(28)	8801(14)	2065(25)	19(7)
C(52)	5713(31)	8953(12)	1176(28)	21(8)
C(53)	4844(37)	9048(15)	764(33)	38(9)
C(54)	4044(35)	9030(14)	1215(32)	32(9)
C(55)	3952(35)	8877(14)	2111(32)	37(9)
C(56)	4961(32)	7995(13)	3344(29)	24(8)
C(57)	5488(25)	7749(10)	3894(23)	6(6)
C(58)	5622(39)	7398(16)	3702(36)	43(9)
C(59)	5190(34)	7248(14)	2935(32)	31(9)
C(60)	4586(32)	7475(13)	2249(29)	23(8)
C(61)	4537(38)	7855(16)	2542(36)	43(9)
C(62)	3470(28)	8562(12)	3959(26)	16(7)
C(63)	3167(32)	8918(13)	4364(30)	26(8)
C(64)	2140(29)	8995(12)	4489(27)	19(8)
C(65)	1511(34)	8683(14)	4351(31)	35(9)
C(66)	1764(31)	8361(13)	3943(29)	25(8)
C(67)	2753(25)	8303(11)	3794(24)	8(7)
C(68)	5983(30)	8730(13)	7208(28)	26(8)
C(69)	6999(25)	8746(12)	7299(23)	13(7)
C(70)	7491(32)	8670(13)	8048(30)	28(9)
C(71)	7023(37)	8528(15)	8768(35)	42(9)
C(72)	6013(35)	8475(14)	8731(33)	34(9)
C(73)	5511(48)	8513(19)	7997(45)	68(9)
C(74)	3993(30)	8738(14)	6433(27)	25(8)
C(75)	3733(32)	8365(13)	6053(29)	25(8)
C(76)	2697(35)	8258(13)	6195(33)	28(8)
C(77)	2085(34)	8472(14)	6647(31)	32(9)
C(78)	2415(31)	8843(13)	6986(28)	28(8)
C(79)	3316(28)	8997(12)	6910(26)	15(7)
C(80)	5263(27)	9427(12)	6607(26)	14(7)
C(81)	5548(45)	9534(18)	7383(42)	60(10)
C(82)	5474(42)	9972(17)	7583(38)	47(9)
C(83)	5117(66)	10219(27)	7043(63)	98(7)
C(84)	4800(79)	10067(34)	6407(75)	125(5)
C(85)	4601(63)	9670(26)	5978(56)	95(8)
C(10)′	7247(89)	9930(36)	4721(81)	97(4)
C(11)′	8836(85)	9969(36)	3698(87)	37(4)

[a] Fractional coordinates are × 10^4

[b] Isotropic values for those atoms refined anisotropically are calculated using the formula given by W. C. Hamilton, *Acta Crystallogr.*, *12* (1959) 609.

TABLE 5

Selected bond distances (Å) and angles (°) for $(Me_2N)_2Zr[H_6Re(PPh_3)_2]_2$

(a) Distances			
Re(2)	Zr(1)	2.819(4)	
Re(2)	P(6)	2.422(12)	
Re(2)	P(7)	2.385(11)	
Re(3)	Zr(1)	2.863(4)	
Re(3)	P(4)	2.425(12)	
Re(3)	P(5)	2.421(12)	
Zr(1)	N(8)	2.03(4)	
Zr(1)	N(9)	2.06(3)	
(b) Angles			
Zr(1)	Re(2)	P(6)	127.81(27)
Zr(1)	Re(2)	P(7)	121.6(3)
P(6)	Re(2)	P(7)	110.6(4)
Zr(1)	Re(3)	P(4)	120.8(3)
Zr(1)	Re(3)	P(5)	126.9(3)
P(4)	Re(3)	P(5)	112.3(4)
Re(2)	Zr(1)	Re(3)	117.27(15)
Re(2)	Zr(1)	N(8)	108.6(10)
Re(2)	Zr(1)	N(9)	109.5(9)
Re(3)	Zr(1)	N(8)	108.4(10)
Re(3)	Zr(1)	N(9)	111.5(9)
N(8)	Zr(1)	N(9)	100.1(14)
Zr(1)	N(8)	C(10)	120.4
Zr(1)	N(8)	C(11)′	128.8
C(10)	N(8)	C(11)′	109.9

even on cooling to −85 °C, although some broadening of the resonances does occur. The $^{31}P\{^1H\}$ NMR spectrum of (I) and of (II) consists of a singlet.

Single crystals of (I) were successfully grown from toluene and pentane. An X-ray diffraction study (Figs. 1 and 2) reveals the geometry about Zr to be distorted tetrahedral, and rather similar to that in $(C_5H_5)_2Zr(Cl)[H_3Os(PMe_2Ph)_3]$ [5]. The diffraction data did not reveal the locations of the hydride ligands. The Zr–Cl distance, 2.508(7) Å, is significantly longer than in $(C_5H_5)_2ZrCl_2$ (2.441(5) Å) [17], consistent with diminished $Cl \rightarrow Zr$ π-donation in the hexahydride (I).

The $Re(PPh_3)_2$ moiety in (I) is similar to that in $Re_2H_8(PPh_3)_4$ [18], although (I) has slightly longer Re—P bonds (averaging 2.388 Å *versus* 2.332 Å for $Re_2H_8(PPh_3)_4$) and a slightly smaller P—Re—P angle (102.6° *versus* 105.2° for $Re_2H_8(PPh_3)_4$ [18]. As shown in Fig. 2, the rotational conformation about the Zr–Re vector has the C_5H_5 and PPh_3 groups staggered. However, the NMR equivalence of the phosphines requires facile rotation about the Zr–Re vector.

$ReH_7(PPh_3)_2$ also reacts with 1 equiv $Zr(NMe_2)_4$ to form $(NMe_2)_3Zr[H_6Re(PPh_3)_2]$ (III) and $HNMe_2$. Even more significantly, $Zr(NMe_2)_4$ reacts with 2 equiv $ReH_7(PPh_3)_2$ to form $(NMe_2)_2Zr[H_6Re$-

$(PPh_3)_2]_2$ (IV) and 2 equiv $HNMe_2$. This contrasts with $(C_5H_5)_2Zr(NMe_2)_2$ which only reacts to form the mono-elimination product (II) even in the presence of an excess of $ReH_7(PPh_3)_2$. Both (III) and (IV) are air-sensitive solids which are insoluble in saturated hydrocarbons and soluble in common aromatic solvents. As with compounds (I) and (II), the ^{1}H NMR spectra of (III) and (IV) both show a triplet hydride resonance, due to rapidly fluxional hydride ligands.

A single-crystal X-ray diffraction study (Fig. 3) reveals the coordination about the Zr in (IV) is distorted tetrahedral (2N, 2Re). The NMe_2 groups are planar and the terminal Zr—N bond lengths are the same as those in $Zr(NMe_2)_4$ within experimental error [19]. The planes defined by the two amido groups are nearly orthogonal (71°) with respect to each other. The $Re(PPh_3)_2$ moieties are very similar to each other and the angle between the two P—Re—P planes is 108°. In contrast to compound (I), both Re centers in (IV) are coplanar with the attached Zr and P atoms. This is achieved with a larger P—Re—P angle (110.6° and 112.3°) and probably reflects diminished P/ZrL repulsion when L changes from C_5H_5 to NMe_2.

The reactivity of (I) and (III) with CO and CO_2 has been examined. As a basis for comparison, $(C_5H_5)_2Zr(H)[H_6Re(PMePh_2)_2]$ (V) and $(C_5H_5)_2Zr(H)$-$[H_3Os(PMe_2Ph)_3]$ (VI) were also subjected to reaction with CO and CO_2. Neither (I), (III), (V) nor (VI) react with CO under mild conditions (1 atm CO, 25 °C). Compound (V) also failed to react under 10 atm at room temperature.

Under 1 atm CO_2 at 25 °C, (I) can be recovered unchanged, but (III) does react. The primary product when a deficiency of CO_2 reacts with $(Me_2N)_3Zr[H_6Re(PPh_3)_2]$ shows ^{1}H NMR signals at 3.30 (s) ppm and -4.24 (t, $J = 12$ Hz) ppm. This product transformed over a 15 h period in benzene to form $(NMe_2)_2Zr[H_6Re(PPh_3)_2]_2$ (IV) and $Zr(O_2CNMe_2)_4$ [20], both of which were identified by comparison with authentic samples.

$(C_5H_5)_2Zr(H)[H_6Re(PMePh_2)_2]$ also reacted with CO_2 to yield the formate complex $(C_5H_5)_2Zr(O_2CH)[H_6Re(PMePh_2)_2]$. The formate hydrogen appears at 8.59 ppm and there is a strong infrared absorbance at 1640 cm^{-1}, indicative of a monodentate binding mode. $(C_5H_5)_2Zr(H)[H_3Os(PMe_2Ph)_3]$ also reacted to insert CO_2 into the Zr—H bond.

Discussion

Synthetic aspects

The reaction of $ReH_7(PPh_3)_2$ with zirconium amides represents the extension of bimolecular amine elimination to the formation of polyhydride compounds incorporating both early and late transition metals. Crucial to the success of this class of reaction is the acidic nature of the hydride. Norton and coworkers have observed proton transfer in the reaction between $MoH(CO)_3(C_5H_5)$ and $(C_5H_5)_2ZrMe_2$ [21]. We have also observed that

$WH_4(PMePh_2)_4$ does not react with $[Zr(NMe_2)_4]_2$ which supports the hypothesis of a proton-transfer mechanism, since hydride acidity increases from left to right across the Periodic Table. Also supporting this hypothesis is the observation that all successful examples of amine elimination reactions involve hydrides which have significant proton acidity [22].

When $(C_5H_5)_2Zr(NMe_2)_2$ was reacted with $ReH_7(PPh_3)_2$, only 1 equiv dimethylamine was eliminated to form (**II**), even in the presence of excess $ReH_7(PPh_3)_2$. Yet, under the same conditions, the reaction between $[Zr(NMe_2)_4]_2$ and $ReH_7(PPh_3)_2$ results in elimination of 2 equiv dimethylamine to form (**IV**). Comparison with other examples of amine elimination reactions involving Group IV transition metal amides leads us to suspect the extent of reaction is more sterically than electronically controlled [11, 12].

Structural aspects

The most obvious question one might hope to answer on the basis of our X-ray diffraction studies is the extent of metal–metal interaction between zirconium and rhenium. This question is complicated, however, by our inability to locate the hydride ligands based on the X-ray diffraction data. In related Re–Al compounds [9], evidence for both bridging and terminal hydrides were observed. We feel it is quite likely that both bridging and terminal hydrides are present in these Zr–Re compounds as well. The bridging and terminal hydrides must be close in energy as demonstrated by the fact that all the hydrides are rapidly fluxional on the NMR timescale, even at −80 °C.

Given the likelihood of bridging hydrides, no conclusions about the strength of metal–metal interaction may be drawn from the Zr–Re distances. The fact that the Zr–Re distance in (**IV**) is shorter than that in (**I**) by *ca.* 0.15 Å could be explained by increased electron deficiency as zirconium caused by replacing a cyclopentadienyl group in (**I**) (a five-electron donor) with a dimethylamido group (a three-electron donor) in (**IV**). Alternatively, it could be argued that replacing at cyclopentadienyl group [in (**I**)] with a dimethylamido group [in (**IV**)] results in more vacant molecular orbitals on zirconium and, therefore, more bridging hydrides in (**IV**) than in (**I**). The increased number of bridging hydrides would also be expected to decrease the Zr–Re distance. Our data does not permit us to distinguish between these explanations.

As previously mentioned, the two NMe_2 groups on (**IV**) are nearly orthogonal. This is probably a result of the NMe_2 moieties (which are strong π-donors [23]) assuming rotational conformations which minimize competition for orbitals into which to donate π-electron density.

It was hoped that these heterometallic polyhydrides would provide a method of activating CO. However, no reactions were observed with CO. In general, the reactions observed appear to be localized on the individual mononuclear transition metal moieties. Carbon dioxide inserts into the Zr—H bond in (**V**) to produce a formate–Zr–Re compound. Floriani *et al.* have reported a similar reaction in which $(C_5H_5)_2Zr(H)Cl$ reacted with CO_2 to give

$[(C_5H_5)_2ZrCl]_2O$ and formaldehyde [24]. They proposed that in this reaction $(C_5H_5)_2Zr(O_2CH)Cl$ is an intermediate which reacts with further $(C_5H_5)_2Zr(H)Cl$ to give the final products. The effect of the $H_6Re(PMePh_2)_2$ moiety, then, is to stabilize the product of CO_2 insertion. In the reaction of (**III**) with CO_2, the latter rapidly inserts into the Zr—N bonds, as is typical of mononuclear zirconium amides. The initially-formed product subsequently underwent a further slow redistribution reaction, resulting in the production of $Zr(O_2CNMe_2)_4$ and $Zr(NMe_2)_2[H_6Re(PPh_3)_2]_2$. Given the precedent for facile insertion of CO_2 into Zr—N bonds in $[Zr(NMe_2)_4]_2$ [20], it would seem logical to propose that the initially-formed species is $Zr(O_2CNMe_2)_3[H_6Re(PPh_3)_2]$. This heterometallic carbamate then undergoes disproportionation to $Zr(O_2CNMe_2)_4$ and $(NMe_2)_2Zr[H_6Re(PPh_3)_2]$, driven perhaps by the stability of Zr—O bonds.

Conclusions

We have demonstrated that bimolecular amine elimination can be extended to the production of polyhydride compounds containing both early and late transition metals. When polyamido compounds are used, this method can be extended beyond dimers to result in the logical, stepwise production of heterometallic polyhydride clusters. We have yet to detect evidence for cooperativity between the two transition metal centers in reactions with CO_x substrates. Likewise, elimination of 2 mol $HNMe_2$, with M/M′ multiple bond formation [eqn. (1)] has not yet been accomplished.

The fact that $(C_5H_5)_2Zr(H)[H_6Re(PPh_3)_2]$ and $(C_5H_5)_2Zr(H)[H_3Os(PMe_2Ph)_3]$ fail to react with CO (the former also fails to react with ethylene), together with the fact that these compounds must have sufficient bridging hydrides to saturate their zirconium centers, suggests that prior coordination of CO or C_2H_4 is a necessity for subsequent hydrogenation. The successful reaction of both of these with CO_2 thus implicates a *direct* attack by the hydride terminal on zirconium at the carbon of approaching CO_2; prior coordination of CO_2 is not required for its hydrogenation. Such a mechanism has also been deduced for the reaction of CO_2 with $RW(CO)_5^-$ [25].

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