Synthesis and Characterization of $\{Re(CO)_3\}_{4-n}\{PtMe_3\}_n(OH)_4$, ($n$ = 1−3). A Set of Heterobimetallic Hydroxy Cubane Complexes

Udo Brand, Chris A. Wright, and John R. Shapley*

Department of Chemistry, University of Illinois,
Urbana, Illinois 61081

Received June 15, 1999

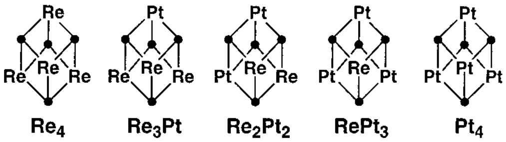
Introduction

As part of their seminal studies of platinum alkyls, Pope and Peachy[1] synthesized the compound later established as the first metallo hydroxy cubane, $[PtMe_3(OH)]_4$.[2−4] More recent examples of hydroxy cubane compounds have been characterized for the elements Cr,[5] Mo,[6] W,[6] Mn,[7] Re,[8−10] Ru,[11−13] Ni,[14] Cu,[15] and Cd.[16] The corner-vacant trinuclear fragment $[NEt_4][Re_3(CO)_9(OH)_4]$[17] (**Re$_3$**) has been used as a tripodal ligand to form heterobimetallic complexes with a fused "double-cubane" structure.[18] We were interested in exploring the use of **Re$_3$** as a starting material for the synthesis of mixed-metal hydroxy cubanes by addition of appropriate $[ML_n]^+$ fragments. Here we report the addition of a $[PtMe_3]^+$ fragment to form a **Re$_3$Pt** cubane as well as extension to the synthesis of analogous **Re$_2$Pt$_2$** and **RePt$_3$** compounds. This results in a complete set of heterobimetallic hydroxy cubane derivatives of the individual homometallic parent complexes (see Chart 1).

Experimental Section

General Procedures. Unless specified otherwise, all reactions were carried out under an atmosphere of nitrogen. All solvents were appropriately dried prior to use. Silver nitrate (Allied Chemical) and sodium hydroxide (Fischer) were used without further purification. The compounds $[PtMe_3I]_4$,[19] $[PtMe_3OH]_4$,[1] $[Re(CO)_3OH]_4$,[9] $[NEt_4]_2[Re(CO)_3Br_3]$,[17] and $[NEt_4][Re_3(CO)_9(OH)_4]$[17] were synthesized by reported procedures. TLC plates were prepared with silica gel (Aldrich, TLC grade 7749), and separations were performed in air. Infrared spectra were recorded on a Perkin-Elmer 1750 FT-IR spectrometer. Both ^1H and ^{195}Pt NMR spectra were obtained on a Varian U500 NMR instrument. Positive-ion fast atom bombardment (FAB) mass spectra, using a 3:1 mixture of dithiothreitol/dithioerythritol (magic bullet) as the dispersing medium, were obtained on a VG ZAB-SE spectrometer by the staff of the Mass Spectrometry Laboratory of the School of Chemical Sciences.

Chart 1



Re = $Re(CO)_3$ ● = μ_3-OH **Pt** = $PtMe_3$

Table 1. Crystallographic Data for **Re$_3$Pt**·$2CH_3COCH_3$ and **RePt$_3$**·$O(CH_2CH_3)_2$

	Re$_3$Pt·$2CH_3COCH_3$	**RePt$_3$**·$O(CH_2CH_3)_2$
empirical formula	$C_{18}H_{25}O_{15}PtRe_3$	$C_{16}H_{41}O_8Pt_3Re$
fw	1235.07	1132.96
space group	$P2_1/n$	$P2_12_12_1$
temp (K)	198(2)	293(2)
a (Å)	11.8513(5)	9.222(2)
b (Å)	16.9887(7)	10.177(2)
c (Å)	14.7834(6)	27.976(6)
α (deg)	90	90
β (deg)	95.8530(10)	90
γ (deg)	90	90
V (Å^3)	2960.9(2)	2625.7(9)
Z	4	4
λ(Mo Kα) (Å)	0.710 73	0.710 73
ρ_{calcd} (g/cm^3)	2.771	2.866
μ(Mo Kα) (cm^{-1})	169.96	205.61
R1[a]	0.0319 [$I > 2\sigma(I)$]	0.0510 [$I > 2\sigma(I)$]
wR2[b]	0.0648	0.1186

[a] $R1 = \sum|(F_o - F_c)|/\sum F_o$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum F_o^4]^{1/2}$.

Synthesis of $\{$Re(CO)$_3\}_3\{$PtMe$_3\}$(OH)$_4$ (Re$_3$Pt). Samples of $[NEt_4][Re_3(CO)_9(OH)_4]$ (25.9 mg, 0.0257 mmol) and $[PtMe_3I]_4$ (9.44 mg, 0.006 43 mmol) were combined in a three-neck flask with acetone (30 mL), and the solution was heated to reflux. A solution of $AgNO_3$ (4.43 mg, 0.0261 mmol) in water (4 mL) was added dropwise to the refluxing solution, which became turbid after a few minutes. The mixture was stirred and heated under reflux for 18 h and then cooled to room temperature and filtered. The solvent was removed in vacuo, and the residue was dissolved in acetone. Separation by TLC (acetone/hexane, 1:2) gave a major band (R_f = 0.4) containing **Re$_3$Pt** (25 mg, 0.022 mmol, 87%). Trace amounts of $\{Re(CO)_3\}_2\{PtMe_3\}_2(OH)_4$ (**Re$_2$Pt$_2$**) eluted prior to **Re$_3$Pt**, and small amounts of $[Re(CO)_3OH]_4$ (**Re$_4$**) eluted after **Re$_3$Pt**. Anal. Calcd for $C_{12}H_{13}O_{13}Re_3Pt \cdot 0.5\ C_3H_6O$: C, 14.09; H, 1.40. Found: C, 14.16; H, 1.34.

Synthesis of $\{$Re(CO)$_3\}\{$PtMe$_3\}_3$(OH)$_4$ (RePt$_3$). Samples of $[NEt_4]_2[Re(CO)_3Br_3]$ (56.7 mg, 0.0736 mmol) and $[PtMe_3I]_4$ (82.8 mg, 0.0564 mmol) were combined in a Schlenk flask with acetone (10 mL). A solution of $AgNO_3$ (75.8 mg, 0.446 mmol) in water (5 mL) was added slowly to the stirred solution, which quickly clouded with precipitate. The mixture was stirred further for 3 h and then filtered. A 1 mL portion of NaOH solution (0.446 M) was added to the filtrate, and the solution was stirred for 30 min. The solution was concentrated to 5 mL in vacuo and then extracted with three 10 mL portions of diethyl ether. The ether phase was dried in vacuo. The residue was dissolved in ether and separated from the mixture by TLC (ether/hexane, 1:2), to give a major band (R_f = 0.35) containing **RePt$_3$**. Recrystalli-

---

(1) Pope, W. J.; Peachey, S. J. *J. Chem. Soc.* **1909**, 571.
(2) Cowan, D. O.; Krieghoff, N. G.; Donnay, G. *Acta Crystallogr.* **1968**, *B24*, 287.
(3) Spiro, T. G.; Templeton, D. H.; Zalkin, A. *Inorg. Chem.* **1968**, *7*, 2165.
(4) Preston, H. S.; Mills, J. C.; Kennard, C. H. L. *J. Organomet. Chem.* **1968**, *14*, 447.
(5) McNeese, T. J.; Mueller, T. E.; Wierda, D. A.; Darensbourg, D. J.; Delord, T. J. *Inorg Chem.* **1985**, *24*, 3465.
(6) Lin, J. T.; Yeh, S. K.; Lee, G. H.; Wang, Y. *J. Organomet. Chem.* **1989**, *361*, 89.
(7) Horn, E.; Snow, M. R.; Zeleny, P. C. *Aust. J. Chem.* **1980**, *33*, 1659.
(8) Herberhold, M.; Süss, G. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 700.
(9) Herberhold, M.; Süss, G.; Ellermann, J.; Gäbelein, H. *Chem. Ber.* **1978**, *111*, 2931.
(10) Nuber, B.; Oberdorfer, F.; Ziegler, M. L. *Acta Crystallogr., Sect. B* **1981**, 2062.
(11) Hörnig, A.; Englert, U.; Koelle, U. *J. Organomet. Chem.* **1993**, *453*, 255.
(12) Suzuki, H.; Kakigano, T.; Igarashi, M.; Usui, A.; Noda, K.; Oshima, M.; Tanaka, M.; Moro-Oka, Y. *Chem. Lett.* **1993**, 1707.
(13) Gould, R. O.; Jones, C. L.; Robertson, D. R.; Stephenson, T. A. *J. Chem. Soc., Chem. Commun.* **1977**, 222.
(14) Aurivillius, B. *Acta Chem. Scand., Ser. A* **1977**, *31*, 501.
(15) Sletten, J.; Sørensen, A.; Julve, M.; Journaux, Y. *Inorg. Chem.* **1990**, *29*, 5054.
(16) Weidenbruch, M.; Herrendorf, M.; Schäfer, A.; Pohl, S.; Saak, W. *J. Organomet. Chem.* **1989**, *361*, 139.
(17) Alberto, R.; Egli, A.; Abram, U.; Hegetschweiler, K.; Gramlich, V.; Schubiger, P. A. *J. Chem. Soc., Dalton Trans.* **1994**, 2815.
(18) Herrmann, W. A.; Egli, A.; Herdtweck, E.; Alberto, R.; Baumgärtner, F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 432.
(19) Baldwin, J. C.; Kaska, W. C. *Inorg. Chem.* **1975**, *14*, 2020.

10.1021/ic9906914 CCC: $18.00

Table 2. Comparison of Distances (Å) and Angles (deg) for Metallo Hydroxy Cubane Compounds

cmpd	Re−O	Pt−O	Re−O−Re	Re−O−Pt	Pt−O−Pt	O−Re−O	O−Pt−O
Re_4[a]	2.191(24)		104.0(10)			73.9(9)	
Re_{3Pt}[b]	2.173(7)	2.237(7)	104.8(3)	102.9(3)		74.0(3)	73.6(3)
$RePt_3$[b]	2.174(11)	2.220(12)		103.6(5)	100.3(5)	75.9(4)	76.8(4)
Pt_4[c]		2.217(5)			101.6(3)		77.1(4)

[a] Reference 21. [b] This work. [c] Reference 22.

zation from a diethyl ether solution layered with hexane gave the product (40 mg, 0.038 mmol, 51%). Small amounts of $[PtMe_3OH]_4$ (**Pt_4**) eluted prior to **$RePt_3$**, small amounts of **Re_2Pt_2** eluted after **$RePt_3$**, and trace amounts of **Re_3Pt** eluted subsequently. Anal. Calcd for $C_{12}H_{31}O_7RePt_3{\cdot}0.5C_4H_{10}O$: C, 15.33; H, 3.31. Found: C, 15.62; H, 3.41.

Reaction of $[Re(CO)_3OH]_4$ with $[PtMe_3OH]_4$. Samples of **Re_4** (22.5 mg, 0.0196 mmol) and **Pt_4** (20.7 mg, 0.0201 mmol) were combined in a Schlenk flask with acetone (45 mL) and water (5 mL). The solution was stirred under reflux for 6 d. It was then filtered, and the filtrate was dried in vacuo. The residue was separated by TLC (ether/hexane, 1:2) into three bands: **Pt_4** ($R_f = 0.75$, 7.3 mg), **$RePt_3$** ($R_f = 0.55$, 6.4 mg), and a broad mixture of **Re_2Pt_2**, **Re_3Pt**, and **Re_4** ($R_f = 0.41$). This mixed band was subjected to TLC again (ether/hexane, 1:3) and eluted three times to separate a narrow band ahead of the broad band. The narrow band contained **Re_2Pt_2** (2.4 mg, 0.0022 mmol).

X-ray Crystal Structure Determinations. Colorless crystals containing **Re_3Pt** suitable for X-ray diffraction were grown by layering a concentrated acetone/dichloromethane solution with hexane at −20 °C. Colorless crystals containing **$RePt_3$** suitable for X-ray diffraction were grown by layering a concentrated diethyl ether solution with hexane at −20 °C. A summary of selected crystallographic data for **Re_3Pt** and **$RePt_3$** is given in Table 1. Diffraction measurements were made on a Siemens Platform/CCD automated diffractometer using Mo Kα radiation. The structures were solved by direct methods;[20] hydrogen atoms were fixed on calculated positions.

The data were corrected for absorption, and full-matrix least-squares refinement on F^2 of the positional, isotropic thermal, and anisotropic thermal parameters for all non-hydrogen atoms led to satisfactory convergence in each case. A comparison of selected bond lengths and angles is given in Table 2.

Results and Discussion

Syntheses. The reaction of $[NEt_4][Re_3(CO)_9(OH)_4]$ with $[PtMe_3I]_4$ in aqueous acetone in the presence of silver nitrate led to formation of the mixed-metal hydroxy cubane $\{Re(CO)_3\}_3\{PtMe_3\}(OH)_4$ (**Re_3Pt**). The compound was isolated in 87% yield following preparative thin-layer chromatography on silica using acetone/hexane (1:2) as eluent. When 1 equiv amounts of $[PtMe_3I]_4$ and $[NEt_4]_2[Re(CO)_3Br_3]$ are stirred in aqueous acetone with 7 equiv of silver nitrate, the aquo complexes $[PtMe_3(H_2O)_3]^+$ and $[Re(CO)_3(H_2O)_3]^+$ should be formed in a ratio of 4:1. Addition of 5 equiv of NaOH to this mixture provided primarily the expected $\{Re(CO)_3\}\{PtMe_3\}_3(OH)_4$ (**$RePt_3$**). The compound was isolated via thin-layer chromatography on silica and recrystallized from a diethyl ether solution by layering with hexane (51% yield). When a 1:1 combination of the complexes **Pt_4** and **Re_4** was heated for 1 week in refluxing aqueous acetone, a mixture was obtained that showed four signals1 in the ^{195}Pt NMR spectrum. Three of the signals were attributable to the compounds **Pt_4**, **Re_3Pt**, and **$RePt_3$**, and the chemical shift of the fourth signal was suitable for the 2:2 complex $\{Re(CO)_3\}_2\{PtMe_3\}_2(OH)_4$ (**Re_2Pt_2**). We were able to isolate a small amount of **Re_2Pt_2** following extensive thin-layer chromatography. Each of the new heterobimetallic hydroxy cubane complexes showed a characteristic isotope pattern for the molecular ion in the FAB mass spectrum (see Table 3) as well as unique ^1H and ^{195}Pt NMR data (see Table 4). In addition, the structures of **Re_3Pt** and **$RePt_3$** have been established by single-crystal X-ray diffraction studies.

Table 3. Comparison of Molecular Ion Patterns from FAB Mass Spectrometry[a]

Re_{3Pt}			Re_2Pt_2			$RePt_3$		
mass	calc %	obs %	mass	calc %	obs %	mass	calc %	obs %
1114	8	11	1084	9	10	1052	1	4
1115	9	13	1085	17	17	1053	1	4
1116	44	43	1086	47	45	1054	8	11
1117	43	46	1087	68	68	1055	23	28
1118	97	97	1088	100	92	1056	51	53
1119	76	70	1089	96	100	1057	77	75
1120	100	100	1090*	93	92	1058	100	100
1121*	50	49	1091	56	53	1059*	96	98
1122	47	50	1092	37	38	1060	79	75
1123	7	8	1093	15	15	1061	51	54
1124	9	10	1094	10	10	1062	33	31
1125	1	2	1095	1	2	1063	17	22
			1096	1	2	1064	9	10
						1065	3	6
						1066	2	3

[a] The ^{187}Re, ^{195}Pt M^+ peak is marked with an asterisk.

Structures. The molecular structure for **Re_3Pt** is shown in Figure 1. The complex consists of a cubane with one $PtMe_3$ and three $Re(CO)_3$ fragments linked by four μ_3-OH corners. Each metal atom thereby has a distorted octahedral environment composed of three fac carbon atoms (methyl or carbonyl carbon) and three fac oxygen atom donors. The structure has pseudo-3-fold molecular symmetry with the 3-fold axis passing through Pt1 and O4.

The molecular structure of **$RePt_3$** is shown in Figure 2. The cubane complex consists of one $Re(CO)_3$ and three $PtMe_3$ fragments linked by four μ_3-OH corners. Again, each metal atom has a distorted octahedral environment of three fac carbon atoms and three fac oxygen atom donors. The structure also has pseudo-3-fold symmetry with the 3-fold axis passing through Re4 and O1. A comparison of selected bond lengths and angles for the compounds **Re_4**, **Re_3Pt**, **$RePt_3$**, and **Pt_4** is given in Table 2. This comparison shows that the mixing of $Re(CO)_3$ and $PtMe_3$ fragments to form heterometallic hydroxy cubanes causes only slight perturbation to the general structure adopted by these compounds.[21,22] The M−O bond distances are essentially invariant, but the M−O-M and O−M-O angles show smooth variations.

Spectroscopy. Spectroscopic data for the new compounds as well as for the parent compounds **Re_4**[9] and **Pt_4**[22−24] are collected in Table 4. As the number of $Re(CO)_3$ fragments increases, the ν(CO) values also increase, implying that the $Re(CO)_3$ units are electron withdrawing relative to the $PtMe_3$ units. Consistent with this idea, there is a steady downfield shift in hydroxyl proton resonance positions from **Pt_4** to **Re_4**. The coupling constant involving the hydroxyl proton and a ^{195}Pt nucleus also shows a stepwise decline, reflecting the change in local environment from Pt_3 to Pt_2Re to $PtRe_2$. The chemical

---

(20) Sheldrick, G. M. *SHELXTL-PC,* version 5.0; Siemens Industrial Automation, Inc.: Madison, WI, 1994.

Table 4. Spectroscopic Data for Hydroxy Cubane Compounds[a]

cmpd	$\delta(^1H)(OH)$	$^2J_{PtH}$ (Hz)	$\delta(^1H)(CH_3)$	$^2J_{PtH}$ (Hz)	$\delta(^{195}Pt)$[b]	$\nu(CO)$ (cm^{-1})
Pt_4[c]	1.993 (4 H)	11.2	0.899 (36 H)	78.8	−1466	
Pt_3Re	2.494 (1 H)	11.0	0.947 (9 H)	78.4	−1491	2016 (s)
	3.557 (3 H)	8.8	0.970 (18 H)	80.4		1888 (vs, br)
Pt_2Re_2	3.985 (2 H)	8.6	1.044 (12 H)	79.6	−1512	2017 (s)
	4.883 (2 H)	6.2	1.038 (6 H)	81.3		1900 (vs, br)
$PtRe_3$	5.331 (3 H)	6.3	1.135 (9 H)	81.4	−1531	2023 (s)
	6.173 (1 H)					1916 (vs, br)
Re_4[d]	6.635 (4 H)					2029 (s)
						1923 (vs, br)

[a] In acetone or acetone-d_6. [b] Referenced to an external solution of $NaPtCl_6$ in D_2O. [c] Literature NMR values: ^1H NMR (C_6H_6) δ 0.85 ($^2J_{Pt-H}$ = 78.8 Hz), −1.52 ($^2J_{Pt-H}$ = 11.3 Hz);[23] ^1H NMR (C_6D_6) δ 0.84 ($^2J_{Pt-H}$ = 78.8 Hz), −1.50 ($^2J_{Pt-H}$ = 11.4 Hz); ^{195}Pt NMR (C_6D_6) −1511 ppm, (acetone-d_6) −1453 ppm;[24] ^1H NMR ($CDCl_3$) δ 0.90 ($^2J_{Pt-H}$ = 78.3 Hz), −0.53.[22] [d] Literature values: ^1H NMR (acetone-d_6) δ 6.50; IR (THF) $\nu(CO)$ 2021 (s), 1919 (vs) cm^{-1}.[9]

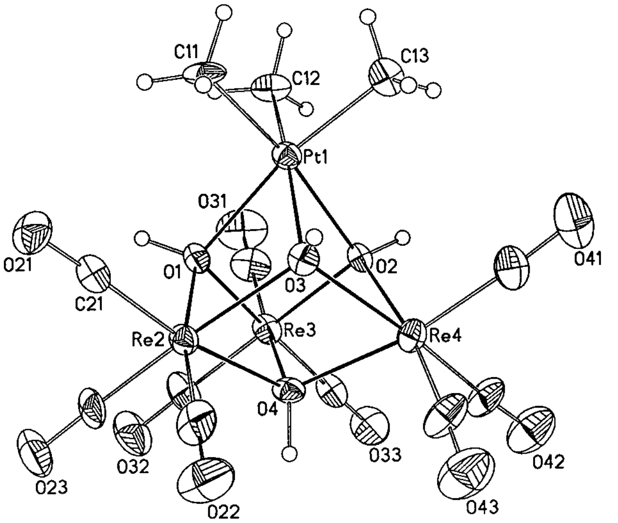


Figure 1. Structural diagram of **Re_3Pt** showing the atomic labeling scheme (35% thermal ellipsoids). Hydrogen atoms are shown in calculated positions. Selected bond lengths (Å): Pt(1)−O(1) = 2.226(7), Pt(1)−O(2) = 2.226(7), Pt(1)−O(3) = 2.258(7), Re(2)−O(1) = 2.164(7), Re(2)−O(3) = 2.169(7), Re(2)−O(4) = 2.160(7), Re(3)−O(1) = 2.156(7), Re(3)−O(2) = 2.169(7), Re(3)−O(4) = 2.195(7), Re(4)−O(3) = 2.198(7), Re(4)−O(4) = 2.173(7).

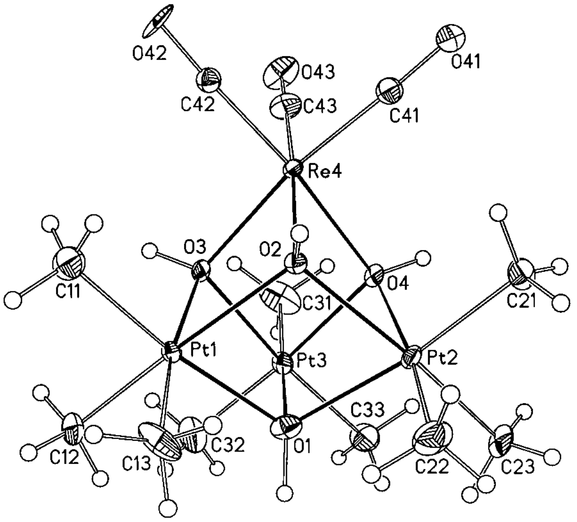


Figure 2. Structural diagram of **$RePt_3$** showing the atomic labeling scheme (35% thermal ellipsoids). Hydrogen atoms are shown in calculated positions. Selected bond lengths (Å): Pt(1)−O(1) = 2.212(12), Pt(1)−O(2) = 2.215(11), Pt(1)−O(3) = 2.232(11), Pt(2)−O(1) = 2.234(13), Pt(2)−O(2) = 2.226(12), Pt(2)−O(4) = 2.229(12), Pt(3)−O(1) = 2.213(12), Pt(3)−O(3) = 2.226(12), Pt(3)−O(4) = 2.218(13), Re(4)−O(2) = 2.207(11), Re(4)−O(3) = 2.165(12), Re(4)−O(4) = 2.150(11).

shifts of the platinum methyl groups also progress downfield with increasing rhenium incorporation, and the $^1H-^{195}Pt$ coupling constant depends systematically on the environment of the trans hydroxyl group. The stepwise increase in coupling as the hydroxyl is shared with more rhenium centers reflects its decreasing donor ability. This “trans influence” effect is often seen for platinum compounds.[25] A comparison of the ^{195}Pt NMR data indicates that as the number of rhenium tricarbonyl fragments increases within the cube, the platinum resonance shifts upfield. Although a number of factors may be involved, the direction of the shift is consistent with the expectation that weaker donors will lead to upfield shifts.[26]

Conclusion. We have synthesized and characterized the set of heterobimetallic hydroxy cubanes $\{Re(CO)_3\}_{4-n}\{PtMe_3\}_n(OH)_4$, ($n$ = 1−3). This set of compounds, in which the ratio of rhenium and platinum varies systematically (3:1, 2:2, 1:3), may prove useful as precursors for the formation of bimetallic metal particles in model heterogeneous catalysts.[27,28]

Acknowledgment. This work was supported by grants from the National Science Foundation (CHE 94-14217) and the Office of Naval Research (N00014-96-1-0494). Purchase of the Siemens Platform/CCD diffractometer by the School of Chemical Sciences was supported by NSF Grant CHE 95-03145. Funding for the instrumentation in the VOICE NMR Lab was provided in part by the W. M. Keck Foundation, the NIH, and the NSF.

Supporting Information Available: X-ray crystallographic files, in CIF format, for **Re_3Pt**$\cdot 2CH_3COCH_3$ and **$RePt_3$**$\cdot O(CH_2CH_3)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC9906914

---

(21) Breimair, J.; Robl, C.; Beck, W. *J. Organomet. Chem.* **1991**, *411*, 395.

(22) Donath, H.; Avtomonov, E. V.; Sarraje, I.; von Dahlen, K.-H.; El-Essawi, M.; Lorberth, J.; Seo, B.-S. *J. Organomet. Chem.* **1998**, *559*, 191.

(23) Morgan, G. L.; Rennick, R. D.; Soong, C. C. *Inorg. Chem.* **1966**, *5*, 372.

(24) Appleton, T. G.; Hall, J. R. *Aust. J. Chem.* **1980**, *33*, 2387.

(25) Pregosin, P. S. *Coord. Chem. Rev.* **1982**, *44*, 247.

(26) Keefer, C. E.; Bereman, R. D.; Purrington, S. T.; Knight, B. W.; Boyle, P. D. *Inorg. Chem.* **1999**, *38*, 2294.

(27) Lane, P. D.; Shapley, J. R. *J. Mol. Catal.* **1994**, *86*, 121.

(28) Nashner, M. S.; Somerville, D. M.; Lane, P. D.; Adler, D. L.; Shapley, J. R.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1996**, *118*, 12964.