

Reactions of Bis(tri-*tert*-butylphosphine)platinum with Metal Hydride Complexes. The Reactions of Pt(P-t-Bu₃)₂ with HRe(CO)₄SbPh₃

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Pt(P-t-Bu₃)₂ reacts with the rhenium hydride complex HRe(CO)₄(SbPh₃), 1, at 25 °C to give the complex PtRe(CO)₄(Ph)(P-t-Bu₃)(μ -SbPh₂)(μ -H), 2, in 75% yield by the oxidative-addition of a Sb-C bond on the SbPh₃ ligand of 1 to a Pt(P-t-Bu₃) group generated by loss of a P-t-Bu₃ ligand from $Pt(P-t-Bu_3)_2$. Compound 2 contains a Pt-Re bond [Pt(1)-Re(1) = 3.0971(7) Å] with a bridging SbPh₂ ligand and a bridging hydrido ligand. At 98 °C, Pt(P-t-Bu₃)₂ reacts with two equivalents of 1 to SbPh₂)₂(µ-H), 4, and PtRe₂(P-t-Bu₃)(µ-SbPh₂)₂(µ-SbPh), 5. Compounds 3 and 4 both contain five-membered Re₂Sb₂Pt rings formed from two mutually bonded Re(CO)₄ groups and two bridging SbPh₂ ligands that are both bonded to the Pt atom. Compound **4** was obtained from **2** independently by reaction with 1. Pt(P-t-Bu₃)₂ reacts with 1 at 68 °C under a hydrogen atmosphere to yield 2, 4, and the new compound, $HPtRe_2(CO)_8(P-t-Bu_3)(\mu-SbPh_2)_2(\mu-H)$, 6, which also contains a five-membered Re₂Sb₂Pt ring similar to those found in **3** and **4**. Five compounds were obtained in low yields when **2** was thermally decomposed under nitrogen at 100 °C: 5 (4%); Re₂(CO)₈(µ-SbPh₂)₂, 7 (6% yield); RePh(CO)₄SbPh₃, **10** (4%); Re₂(CO)₈[PtH(CO)(P-t-Bu₃)](u₃-SbPh)(u-SbPh₂), **11** (4%); RePh-(CO)₄[PtH(CO)P(t-Bu)₃](µ-SbPh₂), **12** (7%). Of these, only **12** is new. Compound **12** is a CO adduct of 2 and was obtained independently by the addition of CO to 2. The CO ligand was added to the platinum atom, the Pt-Re bond of 2 was cleaved, and the phenyl group was shifted to the rhenium atom. The two metal atoms are linked solely by the bridging SbPh₂ ligand. Seven compounds, 5 (9% yield), 7 (26%), Pt₃(CO)₃(P-t-Bu₃)₃, 9 (71%), 11 (7%), 12 (8%), PtRe₂(CO)₉P(t-Bu)₃(µ-H)₂, 13 (13%), and $\text{Re}_3(\text{CO})_{13}(\mu_3-\text{SbPh})(\mu-\text{SbPh}_2)$, 14 (18%), were obtained when 2 was allowed to react with CO at room temperature. Of these, only compound 14 is new. Compound 14 contains no platinum atoms. The structure of 14 contains two Re(CO)₄ groups linked by a bridging SbPh₂ ligand and a bridging SbPh ligand. The bridging SbPh ligand also contains a pendant Re(CO)₅ group.

Introduction

Mixed-metal cluster complexes have been of interest for their ability to facilitate transformations of hydrocarbyl ligands at bimetallic centers.¹ Bimetallic cluster complexes are of interest for applications in homogeneous catalysis² and as precursors to heterogeneous catalysts.³ Understanding the reactivity of the heteronuclear metal-metal bond is central to the development of these complexes as catalysts.

In previous studies, we have shown that the bis(tri-*tert*butyl)phosphine complexes $M(P-t-Bu_3)_2$, M = Pd or Pt, react with polynuclear metal carbonyl cluster complexes containing metal-metal bonds by dissociating one of their phosphine ligands and then adding the $M(P-t-Bu_3)$ group so formed to one or more of the metal-metal bonds of the cluster complex, e.g., eqs 1 and 2.^{4,5}



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Figure 1. ORTEP diagram of the molecular structure of PtOs- $(CO)_4$ SnPh₃(P-t-Bu₃)((μ -H).⁷

The addition of a bridging Pt(P-t-Bu₃) group to a polynuclear metal carbonyl complex can change the reactivity of that complex. For example, it has been shown that the Pt(P-t-Bu₃) group facilitates CO ligand substitution reactions in $Os_3(CO)_{12}$.⁶ It was also shown that the Pt(P-t-Bu₃) group can activate metal-hydrogen bonds. For example, the addition of Pt(P-t-Bu₃)₂ to solutions of the compounds HM(CO)₄- $SnPh_3$, M = Ru or Os, greatly enhanced their reactivity toward insertion of the alkyne HC₂Ph into the M-H bond. It was shown that the activation of the M-H bond occurs through an association of a Pt(P-t-Bu₃) group to the M-H. Details of this association were revealed by an X-ray crystallographic characterization of the compound PtOs(CO)₄Sn- $Ph_3(P-t-Bu_3)(\mu-H)$, a $Pt(P-t-Bu_3)$ adduct of $HOs(CO)_4(SnPh_3)$. The terminal hydride ligand of the HOs(CO)₄(SnPh₃) was converted into a bridging hydride ligand in the Pt(P-t-Bu₃) adduct, PtOs(CO)₄SnPh₃(P-t-Bu₃)((µ-H), and a Pt-Os bond was formed; see Figure 1.

We have now investigated the reaction of Pt(P-t-Bu₃)₂ with the rhenium hydride complex HRe(CO)₄(SbPh₃), **1**, which is isoelectronic and isostructural to HOs(CO)₄(SnPh₃). Compound **1** also forms a Pt(P-t-Bu₃) addition product, but this reaction is more complex than that involving the HOs(CO)₄-(SnPh₃) complex. In fact, the addition of Pt(P-t-Bu₃) to **1** is accompanied by a chemical transformation involving oxidative addition of an Sb–C bond on the SbPh₃ ligand of **1** to a Pt(P-t-Bu₃) group generated by loss of a P-t-Bu₃ ligand from Pt(P-t-Bu₃)₂ to yield the complex PtRe(CO)₄(Ph)(P-t-Bu₃)-(μ -SbPh₂)(μ -H), **2**. The results of our studies of the reaction of Pt(P-t-Bu₃)₂ with complex **1** are reported herein.

Experimental Section

General Data. Reagent grade solvents were dried by the standard procedures and were freshly distilled prior to use. Infrared spectra were recorded on a Thermo Nicolet Avatar 360 FT-IR spectrophotometer. ¹H NMR and ³¹P{¹H} NMR were recorded on a Varian Mercury 400 spectrometer operating at 400.1 and 161.9 MHz, respectively. ³¹P{¹H} NMR spectra were externally referenced against 85% ortho-H₃PO₄. Mass spectrometric (MS) measurements performed by a direct-exposure probe using electron impact ionization (EI) were made on a VG 70S instrument. Pt(P-t-Bu₃)₂ and SbPh₃ were obtained from Strem and were used without further purification. Product separations were performed by TLC in air on Analtech 0.25 and 0.5 mm silica gel 60 Å F₂₅₄ glass plates.

An Improved Synthesis of HRe(CO)₄SbPh₃, 1. A 65.0 mg amount of Re2(CO)10 was dissolved in 40 mL of benzene. The flask was partially submerged in an ice bath, and the solution was irradiated (UV-vis) by using a high-pressure mercury UV lamp (American Ultraviolet Company, 1000 W) at the 250 wpi setting while purging with H_2 at 1 atm for 30 min. A 140 mg sample of SbPh₃ was then added to the solutions, and the irradiation was continued for another 15 min. The solvent was removed in vacuo, and the products were then isolated by TLC by using a 5:1 hexane/methylene chloride solvent mixture to yield in order of elution the following: a colorless band of HRe-(CO)₄SbPh₃,⁸ 1, 79.2 mg (61%), and a colorless band of HRe-(CO)₃(SbPh₃)₂, 16.9 mg (9%). Spectra for HRe(CO)₃(SbPh₃)₂: IR ν_{CO} (cm⁻¹ in hexane): 2016(vs), 1938(m), 1929(m). ¹H NMR (CD₂Cl₂, in ppm): δ 7.4–7.1 (m, 30H, Ph), –5.7 (s, 1H, hydride). Anal. Calcd: 47.93, C; 3.20, H. Found: 47.63, C; 3.19, H.

Synthesis of PtRe(CO)₄(Ph)(P-t-Bu₃](μ -SbPh₂)(μ -H), 2. A 29.8 mg (0.0497 mmol) amount of Pt(P-t-Bu₃)₂ was added to a solution of 22.5 mg (0.0345 mmol) of 1 dissolved in 25 mL of hexane, and the mixture was allowed to stir at room temperature for 1 h. The solvent was removed *in vacuo*, and the product was then isolated by TLC using a 3:1 hexane/methylene chloride elution solvent mixture to yield a yellow band of PtRe(CO)₄-(Ph)(P-t-Bu₃)(μ -SbPh₂)(μ -H), 2, 26.7 mg (75% yield). Spectral data for 2: IR (ν_{CO} in hexane, cm⁻¹): 2081(m), 1987(vs), 1953(s). ¹H NMR (400 MHz, CD₂Cl₂, 25 °C, TMS): δ 6.8–7.5 (m, Ph, 15H), 1.5 (d, Bu^t, 27H, ²J_{P-H} = 12 Hz), -13.5 (d, hydride, 1H, ²J_{P-H} = 11 Hz, ¹J_{105Pt-H} = 429.1 Hz). ³¹P NMR: δ 68.3 (s, P, ¹J_{Pt-P} = 3411 Hz) ppm. Anal. Calcd: C 38.89, H 4.13. Found: C 39.11, H 4.26.

Reaction of Pt(P-t-Bu₃)₂ with 1 at 98 °C. A 23 mg (0.0384 mmol) portion of $Pt(PBu_{3}^{t})_{2}$ was added to a solution of 23.2 mg (0.356 mmol) of ReH(CO)₄SbPh₃ dissolved in 25 mL of heptane, and the mixture was heated to reflux for 2 h. The solvent was removed in vacuo, and the products were then isolated by TLC using a 4:1 hexane/methylene chloride solvent mixture to yield the following in order of elution: a yellow band of 2, 1.2 mg (3%) by Re), a colorless band of $\text{Re}_2(\text{CO})_8(\mu-\text{SbPh}_2)_2$,⁹ 1.8 mg (9%) yield), a yellow band of PtRe2(CO)8[PH(t-Bu2)](Ph)(µ-SbPh2)2- $(\mu$ -H), 3, 2.8 mg (10%), an orange band of PtRe₂(CO)₈(SbPh₃)- $(Ph)(\mu$ -SbPh₂)₂(μ -H), 4, 1.5 mg (5% yield), and an orange band of the known compound PtRe₂(P-t-Bu₃)(µ-SbPh₂)₂(µ-SbPh), 5, 2.1 mg (7% yield). Spectral data for 3: IR (ν_{CO} in hexane, cm⁻¹): 2094(s), 2073(m), 2006(vs), 1999(s), 1988(s), 1980(m), 1968(w), 1957(s) cm⁻¹. ¹H NMR (400 MHz, CD_2Cl_2 , 25 °C, cm^{-} 1968(w), 1957(s) cm⁻¹. TH INMK (400 MHZ, CD₂Cl₂, 25° C, TMS): δ 6.4–7.5 (m, Ph, 25H), 4.5 (d, P–H, 1H, ¹J_{P–H} = 356 Hz, ²J_{195Pt–H} = 18 Hz), 0.9 (d, t-Bu, 18H, ²J_{P–H} = 15 Hz), -13.0 (d, 1H, ³J_{195Pt–H} = 40 Hz, ⁴J_{P–H} = 4 Hz). ³¹P NMR: δ 36.8 (d, P, ¹J_{Pt–P} = 3059 Hz, ¹J_{H–P} = 387 Hz). MS EI/MS: *m*/z 1568 (M⁺), 1540 (M⁺ – CO), 1490 (M⁺ – CO, – C₆H₆). The isotope distribution pattern is consistent with the presence of two rhenium, one platinum, and two antimony atoms. Spectral data for 4: IR (ν_{CO} in hexane, cm⁻¹): 2094(s), 2073(w), 2006(vs), 1999(s), 1989(s), 1979(m), 1968(w), 1956(m) cm⁻¹. ^fH NMR (400 MHz, CD₂Cl₂, 25 °C, TMS): δ 6.8-7.5 (m, Ph, 40H), -12.8 (s, 1H, ${}^{1}J_{Pt-H} = 53$ Hz) ppm. MS EI/MS: m/z 1774 (M⁺), 1718 (M⁺ - 2CO), 1696 (M⁺ - C₆H₆). The isotope distribution

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pattern is consistent with the presence of two rhenium, one platinum, and three antimony atoms.

Reaction of Pt(P-t-Bu₃)₂ with 1 under an Atmosphere of Hydrogen at 68 °C. A 16.9 mg amount of Pt(P-t-Bu₃)₂ was added to a solution of 31.7 mg of HRe(CO)₄(SbPh₃) dissolved in 25 mL of hexane, and the mixture was allowed to reflux for 3 h while purging with H₂. The solvent was removed in vacuo, and the products were then isolated by TLC by using a 4:1 hexane/ methylene chloride solvent mixture to yield the following in order of elution: a yellow band of 2, 7.2 mg (14% yield), an orange band of HPtRe₂(CO)₈(P-t-Bu₃)(μ -SbPh₂)₂(μ -H), 6, 8.0 mg (21% yield), and a yellow band of 4, 2.2 mg (5% yield). Spectral data for 6: IR (ν_{CO} in hexane, cm⁻¹): 2094(m), 1971(w), 2005(vs), 1998(s), 1987(m), 1977(w), 1965(vw), 1954(m) cm⁻¹. ¹H NMR (400 MHz, CD₂Cl₂, 25 °C, TMS): δ 7.0-7.7 (m, Ph, 15H), 1.3 (d, t-Bu, 27H, ${}^{2}J_{P-H} = 12$ Hz), -9.9 (d, hydride, 1H, ${}^{1}J_{195pt-H} = 912$ Hz, ${}^{2}J_{P-H} = 13$ Hz), -13.0 (d, 1H, ${}^{3}J_{195pt-H} = 28$ Hz, ${}^{4}J_{P-H} = 10$ Hz). ${}^{31}P$ NMR: δ 102.1 (s, P, ${}^{1}J_{195pt-P} = 3401$ Hz). MS EI/MS: 1548 (M⁺), 1518 (M⁺ - H₂, -CO), 1491 (M⁺ - H, -2CO), 1470 (M⁺ - C₆H₆) m/z. The isotope distribution pattern is consistent with the presence of two rhenium, one platinum, and two antimony atoms.

Addition of 1 to 2. 1 (34.8 mg, 0.0534 mmol) was added to 43.3 mg (0.0413 mmol) of 2 dissolved in 50 mL of hexane, and the mixture was heated to reflux for 1.5 h. The solvent was removed *in vacuo*, and the products were separated by TLC using a 4:1 hexane/methylene chloride solvent mixture to give in order of elution a yellow band of 2, 13.0 mg (30% recovered), a colorless band of 1, 4.6 mg (13%), a colorless band of Re₂(μ -SbPh₂)₂-(CO)₈, ⁹ 7, 2.1 mg (9% yield), a yellow band of Re₂(μ -H)(μ -SbPh₂)SbPh₃(CO)₇, ⁸ 8, 2.9 mg (12% yield), an orange band of 4, 12.8 mg (18% based on 2), and Pt₃(CO)₃(P-*t*-Bu₃)₃, ¹¹ 9, 2.8 mg (5% yield).

Thermal Decomposition of 2 at 100 °C. A 16.2 mg sample of 2 was dissolved in toluene- d_8 and placed in a sealed NMR tube under nitrogen. The tube was heated in an oil bath for 1 h. The formation of benzene was confirmed in the ¹H NMR spectrum of the solution. The products were then separated by TLC to vield in order of elution a colorless band of the known compound $\text{Re}_2(\text{CO})_8(\mu\text{-SbPh}_2)_2, 7, 90.5 \text{ mg}(6\%)$, a colorless band of the known compound $RePh(CO)_4SbPh_3$, 10,⁸ 0.5 mg (4%), a colorless band of the known compound Re2(CO)8[PtH(CO)(Pt-Bu₃)](μ_3 -SbPh)(μ -SbPh₂), 11, ¹⁰ 0.5 mg (4%), an orange band of the known compound $PtRe_2(P-t-Bu_3)(\mu-SbPh_2)_2(\mu-SbPh)$, 5,¹⁰ 0.5 mg (4%), and a brown band of RePh(CO)₄[PtH(CO)P- $(t-Bu)_3](\mu-SbPh_2), 12, 1.2 \text{ mg} (7\%)$. Spectral data for 12: IR (ν_{CO} in hexane, cm⁻¹): 2072(m), 2034(br), 1981(s), 1966(vs), 1938(m). ¹H NMR (400 MHz, C₆D₆, rt, TMS): δ 7.0–8.3 (m, Ph, 15H), 1.0 (d, t-Bu, 27H, ${}^{2}J_{P-H} = 13$ Hz), -3.8 (d, hydride, 1H, ${}^{1}J_{195Pt-H} = 750$ Hz, ${}^{2}J_{P-H} = 14$ Hz). ${}^{31}P$ NMR: δ 94.8 ppm (${}^{1}J_{195Pt-P} = 2534$ Hz). MS EI/MS: 1148 (Re2(CO)8(SbPh2)2), 1148 (Re2(CO)8- $(SbPh_2)_2 - CO)$, 1076 (M⁺ – H), 972 (M⁺ – Ph, -CO) m/z. The isotope distribution pattern is consistent with the presence of one rhenium, one platinum, and one antimony atoms.

Reaction 2 with CO. Under nitrogen, 14.0 mg of **2** was dissolved in benzene- d_6 in an NMR tube. Then 300 μ L of CO was added to the tube via syringe. The tube was shaken and then allowed to sit at room temperature for 12 h. A ¹H NMR spectrum after this time showed that all of the signals for **2** had disappeared. The solution was transferred to a flask. The solvent was removed *in vacuo*, and the products were separated by TLC using 4:1 hexane/methylene chloride solvent mixture to yield in order of elution a yellow band of the known compound PtRe₂(CO)₉P(*t*-Bu)₃(μ -H)₂,¹² **13**, 0.9 mg (13%), a colorless band

of Re₂(CO)₈(μ -SbPh₂)₂, 7, 2.0 mg (26%), a yellow band of Re₃(CO)₁₃(μ_3 -SbPh)(μ -SbPh₂), 14, 1.1 mg (18%), a colorless band of 11, 0.7 mg (7%), an orange band of 5, 1.1 mg (9%), a yellow band of 12, 1.1 mg (8%), and a yellow band of 9, 4.0 mg (71%). Spectral data for 14: IR (ν_{CO} in hexane, cm⁻¹): 2126(m), 2077(vw), 2062(vs), 2034(vs), 2030(s), 2025(s), 2006(s), 1996(m), 1991(m), 1984(vs), 1974(s), 1952(s). ¹H NMR (400 MHz, COC₂D₆, rt, TMS): δ 7.2–7.7 (m, Ph, 15H) ppm. MS EI/MS: 1398 (M⁺), 1370 (–CO), 1342 (M⁺ – 2CO), 1314 (M⁺ – 3CO), 1286 (M⁺ – 4CO), 1258 (M⁺ – 4CO), 1230 (M⁺ – 4CO) *m/z*. The isotope distribution pattern is consistent with the presence of one antimony and three rhenium atoms.

Conversion of 4 to 3. A 6.0 μ L (0.0324 mmol) portion of PH(t-Bu)₂ was added to 63.2 mg (0.356 mmol) of **4** dissolved in 30 mL of hexane, and the mixture was allowed to stir at 25 °C for 15 min. The solvent was then removed *in vacuo*, and the products were separated by TLC using a 4:1 hexane/methylene chloride solvent mixture to yield in order of elution a colorless band of SbPh₃, 6.9 mg (55%), and a colorless band of **3**, 36.4 mg (65%).

Crystallographic Analyses: 2, 3, 4, 6, 12, and 14. Crystals of yellow 2, suitable for X-ray diffraction, were obtained by slow evaporation of solvent from a solution in hexane solvent at room temperature. Crystals of yellow 3, yellow 4, yellow 6, yellow 14, and brown 12 suitable for X-ray diffraction were obtained by slow evaporation of solvent from solutions in methylene chloride/hexane solvent mixtures at -25 °C. Each data crystal was glued onto the end of a thin glass fiber. X-ray intensity data were measured by using a Bruker SMART APEX CCD-based diffractometer by using Mo K α radiation (λ = 0.71073 Å). The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm.13 Correction for Lorentz and polarization effects were also applied with SAINT+. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied using the program SADABS. All structures were solved by a combination of direct methods and difference Fourier syntheses and refined by full-matrix least-squares on F^2 , using the SHELXTL software package.¹⁴ All non-hydrogen atoms were refined with anisotropic thermal parameters. Unless indicated otherwise, the hydrogen atoms were placed in geometrically idealized positions and included as standard riding atoms during the least-squares refinements. Crystal data, data collection parameters, and results of the refinements are listed in Table 1. Compounds 2, 3, 4, and 6 all crystallized in the monoclinic crystal system. The space group $P2_1/n$ was confirmed for 3 and 14 on the basis of the systematic absences observed in the data. The alternative standard setting of the space group $P2_1/n$, $P2_1/c$, was selected for 2 and 4 on the basis of the systematic absences observed in the data for both of these compounds. The space group C2/c was confirmed for 7 on the basis of the systematic absences observed in the data. With Z = 16there are two independent molecules in the asymmetric unit. The hydrido ligands in 2 and 4 were located and refined in the structural analyses using isotropic thermal parameters. The hydrido ligand in 3 was located in difference Fourier maps. The hydrido ligand in 3 was refined by using the constraint M-H equals 1.75 Å. Compounds 6 and 12 crystallized in the triclinic crystal system. The space group $P\overline{1}$ was assumed and confirmed by the successful solution and refinement of the structure. Both hydrido ligands in 6 were located in a difference Fourier map, but H1 was refined by using a bond length constraint M-H equals 1.75 Å. The hydrido ligand in 12 was located and refined in the structural analyses using an isotropic thermal parameter.

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Table 1. Crystallographic Data for Compounds 2, 3, 4, 6, 12, and

	2	3	4
empirical formula	ReSbPtPO ₄ -	Re ₂ Sb ₂ PtPO ₈ -	Re ₂ Sb ₃ PtO ₈ -
	$C_{34}H_{43}$	$C_{46}H_{45}$	$C_{56}H_{41}$
fw	1049.69	1567.78	1774.63
cryst syst	monoclinic	monoclinic	monoclinic
lattice params	10.047(0)	10.0040(4)	12 (000/0)
$a(\mathbf{A})$	10.24/(2)	12.0949(4)	13.6009(8)
$b(\mathbf{A})$	12.01/(3)	33.6607(12)	10.0159(6)
$\mathcal{C}(\mathbf{A})$	30.009(10)	13.10//(4)	40.894(2)
β (deg)	97.681(14)	110, 179(1)	96.358(1)
γ (deg)	90.00	90.00	90.00
$V(\Lambda^3)$	2662 1(19)	5021 8(2)	5526 5(6)
V (A)	$\frac{5002.1(10)}{P2}$	$\frac{3031.6(3)}{P2}$ /n	$P_{1} = \frac{1}{2}$
Z value	$\frac{1}{2}\frac{2}{1}$	$\frac{1}{\Delta} \frac{2}{n}$	$\frac{1}{2}\frac{1}{c}$
$\rho = (g/cm^3)$	1 904	2 070	2 129
$\mu(M_0 K \alpha) (mm^{-1})$	7.916	8 702	8 365
temperature (K)	294(2)	296(2)	294(2)
2θ (deg)	56 68	56 64	56 68
no obsd reflns	7892	9918	10.838
$(I > 2\sigma(I))$	1092	<i>yy</i> 10	10050
no. params	384	555	635
goodness of fit	1.029	1.078	1.069
max. shift in cycle	0.002	0.002	0.001
residuals ^{<i>a</i>} : R_1 : wR_2	0.0298; 0.0777	0.0367: 0.0736	0.0434: 0.0859
absorp corr	1.000/0.360	1.000/0.545	1.000/0.142
max./min.	,	1	,
largest peak in	2.021	1.561	1.394
final diff map $(e^{-}/Å^{3})$			
	6	12	14
	D - CL D4DO		
empirical formula	$C_{1}H_{1}$	C.H.	C.H.
fw	1547 79	1077 70	1307 53
cryst syst	triclinic	triclinic	monoclinic
lattice params	triennie	triennie	monoenne
a(Å)	11 4655(4)	11.3669(5)	12,698(2)
$h(\mathbf{A})$	12,7853(4)	12.0842(6)	17.635(3)
$c(\mathbf{A})$	17.9052(6)	14.5035(7)	16.896(3)
α (deg)	74.631(1)	80.269(1)	90.00
β (deg)	72.235(1)	85.115(1)	101.845(4)
γ (deg)	86.530(1)	70.918(1)	90.00
$V(Å^3)$	2409 59(14)	1854 69(15)	3702 9(10)
snace group	P_{1}^{-1}	P1	$P_{1/n}^{(10)}$
Z value	2	2	4
$\rho_{\rm cole} (g/\rm{cm}^3)$	2.133	1.930	2.507
$u(Mo K\alpha) (mm^{-1})$	9.084	7.820	11.270
temperature (K)	294(2)	294(2)	294(2)
$2\theta_{\rm max}$ (deg)	56.62	56.62	52.74
no. obsd reflns	8953	8100	5313
$(I > 2\sigma(I))$			
no. params	540	410	442
goodness of fit	1.004	1.039	1.022
max. shift in cycle	0.001	0.002	0.001
residuals ^{<i>a</i>} : R_1 ; wR_2	0.0392; 0.0820	0.0227; 0.0552	0.0455; 0.1123
absorp corr, max./min.	1.000/0.619	1.000/0.677	1.000/0.214
largest peak in	1.750	1.004	3.025
final diff map $(e^{-}/Å^{3})$			
$^{a}R_{1} = \sum_{hkl}(F_{obs} -$	$ F_{\text{calc}})/\sum_{hkl} F_{kl} $	$F_{obs} ; wR_2 = [\Sigma$	$\sum_{hkl} w(F_{obs} - $
$F_{\rm calc})^2 / \sum_{\rm hkl} w F_{\rm obs}^2 ^{1/2}$.	$v = 1/\sigma^2(F_{obs})$; GOF = $\left[\sum_{i=1}^{n}\right]$	$ F_{obs} = $
F_{solel}) ² / $(n_{\text{data}} - n_{\text{vari}})$] ^{1/2}			

Results

The compound PtRe(CO)₄(Ph)(P-t-Bu₃)(μ -SbPh₂)(μ -H), **2**, was obtained in 75% yield from the reaction of Pt(P-t-Bu₃)₂ with **1** in a hexane solution at room temperature in 1 h. Compound **2** was characterized by IR and ¹H NMR spectroscopy and by elemental and single-crystal X-ray diffraction analyses. An ORTEP diagram of the molecular structure of **2** is shown in Figure 2. The compound contains



Figure 2. ORTEP diagram of the molecular structure of PtRe-(CO)₄(Ph)(P-t-Bu₃)(μ -SbPh₂)(μ -H), **2**, showing 30% probability thermal ellipsoids. The hydrogen atoms on the ligands are omitted for clarity. Selected bond distances (Å) and angles (deg) are as follows: Pt(1)-Re(1) = 3.0971(7), Pt(1)-C(27) = 2.051(5), Pt(1)-P(1) = 2.3692(13), Pt(1)-Sb(1) = 2.5180(7), Re(1)-Sb(1) = 2.6769(6), Pt(1)-H(1) = 1.65(5), Re(1)-H(1) = 1.84(5); Sb(1)-Re(1)-Pt(1) = 51.078(15), Pt(1)-Sb(1)-Re(1) = 73.120(17), Sb(1)-Pt(1)-Re(1) = 55.802(15), P(1)-Pt(1)-Sb(1) = 171.29(3).

two metal atoms: one of platinum and one of rhenium. The two metal atoms are mutually bonded and are bridged by a SbPh₂ ligand and one bridging hydrido ligand. The Pt-Re bond distance [Pt(1)-Re(1) = 3.0971(7) Å] is significantly longer than the Pt-Re bond distance of 2.9265(3) Å found in the complex PtRe₂(CO)₉(P-t-Bu₃)(µ-SbPh₂)(µ-H), 16, which was obtained from the reaction of $Pt(P-t-Bu_3)_2$ with Re₂-(CO)₈(μ -SbPh₂)(μ -H).¹⁵ The longer length of the Pt-Re bond in 2 is probably due to the presence of the bridging hydride ligand.¹⁶ The hydrido ligand was located and refined in the structure analysis: Pt(1)-H(1) = 1.65(5) Å and Re-(1)-H(1) = 1.84(5) Å. As expected, it exhibits the usual high-field resonance shift in the ¹H NMR spectrum, $\delta =$ -13.5, with suitable couplings to the phosphorus and platinum atoms: ${}^{2}J_{P-H} = 11$ Hz and ${}^{1}J_{195Pt-H} = 429.1$ Hz. Compound 2 contains a phenyl group σ -bonded to the platinum atom; Pt(1)-C(27) = 2.051(5) Å. There is also a bridging SbPh₂ ligand. The Pt-Sb and Re-Sb bond distances [Pt(1)-Sb(1) = 2.5180(7) Å, Re(1)-Sb(1) = 2.6769(6) Å]are similar to the Pt-Sb and Re-Sb bond distances found in 16: Pt(1)-Sb(1) = 2.5160(4) Å and Re(2)-Sb(1) = 2.6863(5) Å.There are four linear terminal carbonyl ligands on the rhenium

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Scheme 1



Figure 3. ORTEP diagram of the molecular structure of PtRe₂-(CO)₈[PH(t-Bu)₂](Ph)(μ -SbPh₂)₂(μ -H), **3**, showing 30% probability thermal ellipsoids. The hydrogen atoms on the ligands are omitted for clarity. Selected interatomic bond distances (Å) and angles (deg) are as follows: Pt(1)–C(49) = 2.068(6), Pt(1)– P(1) = 2.3011(16), Pt(1)–Sb(1) = 2.6029(4), Pt(1)–Sb(2) = 2.6270(4), Re(1)–Sb(1) = 2.7855(4), Re(1)–Re(2) = 3.2863(4), Re(1)–H(1) = 1.748(10), Re(2)–Sb(2) = 2.7829(4), Re(2)– H(1) = 1.753(10); Sb(1)–Pt(1)–Sb(2) = 91.868(13), Sb(1)– Re(1)–Re(2) = 93.759(11), Sb(2)–Re(2)–Re(1) = 90.566(11), Pt(1)–Sb(1)–Re(1) = 125.606(16), Pt(1)–Sb(2)–Re(2) = 122.492(15).

atom and a tri-*tert*-butylphosphine ligand on the platinum atom: Pt(1)-P(1) = 2.3692(13) Å. The SbPh₂ ligand is formally a three-electron donor to the two metal atoms. Formally, the platinum atom in **2** is in a +2 oxidation state and has a 16-electron configuration, and the rhenium atom is in a +1 oxidation state and has an 18-electron configuration.



When the reaction of **1** with Pt(P-t-Bu₃)₂ was performed in a heptane solution at reflux (98 °C), compound **2** was not obtained, but three other compounds were formed: PtRe₂-(CO)₈[PH(t-Bu₂)](Ph)(μ -SbPh₂)₂(μ -H), **3** (10% yield), PtRe₂-(CO)₈(SbPh₃)(Ph)(μ -SbPh₂)₂(μ -H), **4** (5% yield), and PtRe₂-(P-t-Bu₃)(μ -SbPh₂)₂(μ -SbPh), **5**¹⁰ (7% yield). See Scheme 1.

Compounds **3** and **4** are new and were characterized by IR and ¹H NMR spectroscopy and by mass spectrometry and single-crystal X-ray diffraction analyses. Compound **5** was obtained by us previously from the reaction of $\text{Re}_2(\text{CO})_8(\mu$ -SbPh₂)₂ with Pt(P-t-Bu₃)₂.¹⁰ ORTEP diagrams of the molecular

Figure 4. ORTEP diagram of the molecular structure of PtRe₂-(CO)₈(SbPh₃)(Ph)(μ -SbPh₂)₂(μ -H), **4**, showing 30% probability thermal ellipsoids. The hydrogen atoms on the ligands are omitted for clarity. Selected interatomic bond distances (in Å) are as follows: Pt(1)–Sb(1) = 2.5744(5), Pt(1)–Sb(2) = 2.6353(5), Pt(1)–Sb(3) = 2.5612(5), Re(1)–Re(2) = 3.2761(4), Re(1)– Sb(1) = 2.7675(5), Re(2)–Sb(2) = 2.7879(5), Re(1)–H(1) = 1.69(6), Re(2)–H(1) = 1.85(6), Pt(1)–C(1) = 2.059(7); Sb(1)– Pt(1)–Sb(2) = 92.570(15), Pt(1)–Sb(1)–Re(1) = 116.679(19), Pt(1)–Sb(2)–Re(2) = 123.166(17), Sb(1)–Re(1)–Re(2) = 92.135(12), Sb(2)–Re(2)–Re(1) = 93.201(13).

structure of 3 and 4 are shown in Figures 3 and 4, respectively. Both compounds consist of a heterocyclic five-membered ring containing two rhenium atoms and a platinum atom that is linked to the rhenium atoms by two bridging SbPh₂ ligands. The platinum atom is bonded to both SbPh₂ ligands: Pt(1)-Sb(1) = 2.6029(4) Å and Pt(1)-Sb(2) =2.6270(4) Å in 3 and Pt(1)-Sb(1) = 2.5744(5) Å and Pt(1)-Sb(2) = 2.6353(5) Å in 4. These distances are slightly longer than the Pt-Sb distance in the three-membered ring in 2: 2.5180(7) Å. The Re–Sb distances [Re(1)–Sb(1) = 2.7855(4) Å, Re(2)-Sb(2) = 2.7829(4) Å in 3 and Re(1)-Sb(1) =2.7675(5) Å, Re(2)-Sb(2) = 2.7879(5) Å in 4] are also slightly longer than those in 2, 2.6769(6) A. Both compounds were obviously formed by the reaction of Pt(P-t-Bu₃)₂ with two equivalents of 1. It seems likely that compound 2 was an intermediate in this reaction, and this is supported by our study of the reaction of 1 with 2; see below. The two rhenium atoms in 3 and 4 are mutually bonded: Re(1)-Re(2) =3.2863(4) Å in 3 and Re(1)-Re(2) = 3.2761(4) Å in 4. These Re-Re distances are considerably longer than the Re-Re distance in $\text{Re}_2(\text{CO})_{10}$, 3.042(1) Å.¹⁷ The increase in the Re-Re bond length is probably due to the presence of a bridging hydrido ligand across the Re–Re bond in both compounds.¹³

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The Re-Re distances are only slightly longer than the Re-Re distances between the rhenium atoms of the hydride-bridged Re-Re bonds in Re₃(CO)₁₂(μ -H)₃ of 3.241(2) Å.¹⁸ The hydrido ligands were located and refined crystallographically in both compounds [Re(1)-H(1) = 1.748(10) Å, Re(2)-H(1) =1.753(10) Å in 3 and Re(1)-H(1) = 1.69(6) Å, Re(2)-H(1) = 1.85(6) Å in 4], and they exhibit the expected high-field resonance shift in the ¹H NMR spectra [$\delta = -13.0$ (d, 1H, ${}^{3}J_{195Pt-H} = 40$ Hz, ${}^{4}J_{P-H} = 4$ Hz) in 3 and -12.8 (s, 1H, ${}^{1}J_{195Pt-H} = 53$ Hz) in 4]. An interesting, but not unprecedented feature of these hydride ligands is that they lie inside the ring. We have observed this feature previously in fivemembered ReSn ring clusters that we prepared recently.¹⁹ Apparently, when the ring gets sufficiently large (five atoms), the ligand crowding on the outside of the ring is sufficiently large that the small hydrido ligand is accommodated more efficiently on the inside of the ring. As in 2, there is a phenyl ring on the platinum atom: Pt(1)-C(49) = 2.068(6) Å in 3 and Pt(1)-C(1) = 2.059(7) Å in 4. The greatest difference between 3 and 4 is the presence of a P(t-Bu)₂H ligand on the Pt atom of 3 and a SbPh₃ ligand on the Pt atom of 4. The P(t-Bu)₂H ligand was evidently derived from a P(t-Bu)₃ ligand in the Pt(P-t-Bu₃)₂ reagent. The formation of P(t-Bu)₂H ligands from P(t-Bu)₃ ligands has been observed previously and probably involves formally the elimination of an isobutene from one of the tertbutyl groups.²⁰ We found that compound **4** could be converted to 3 in 65% yield by treatment with P(t-Bu)₂H at 25 °C for 15 min. Both rhenium atoms in compounds 3 and 4 are in the +1oxidation state and have 18-electron configurations. The platinum atoms in 3 and 4 are in the +2 oxidation state and have 16-electron configurations.

When 1 was allowed to react with Pt(P-t-Bu₃)₂ in a hexane solution at reflux (68 °C) under an atmosphere of hydrogen (1 atm), three compounds were formed: 2(14% yield), 4(5% yield), and HPtRe₂(CO)₈(P-t-Bu₃)(μ -SbPh₂)₂(μ -H), 6 (21% yield). Compound 6 has been characterized crystallographically, and an ORTEP diagram of its molecular structure is shown in Figure 5. Compound 6 contains a five-membered Re₂Sb₂Pt ring, similar to that in compounds 3 and 4. It is composed of two Re(CO)₄ groups and two bridging SbPh₂ ligands with a HPt(P-t-Bu₃) group between them.



Unlike **3** and **4**, there is no phenyl group on the platinum atom. In **7**, the phenyl group was replaced with a terminal hydride ligand, presumably derived from the hydrogen atmosphere. The phenyl group was probably eliminated as benzene. As in **3** and **4**, there is a bridging hydride ligand across the Re–Re bond on the inside of the five-membered ring. The bridging hydride ligand was located and refined with restraints. The terminal hydride ligand on platinum was located and refined without restraints. The Pt–H bond distance is slightly shorter than the Re–H bond distances: Pt(1)–H(2) = 1.60(9) Å, Re(1)–H(1) = 1.76(1)Å, Re(2)–H(1) = 1.761(10)Å. Both hydride ligands exhibit high-field resonance shifts in the ¹H



Figure 5. ORTEP diagram of the molecular structure of HPtRe₂-(CO)₈(P-t-Bu₃)(μ -SbPh₂)₂(μ -H), **6**, showing 30% probability thermal ellipsoids. The hydrogen atoms on the ligands are omitted for clarity. Selected interatomic bond distances (Å) and angles (deg) are as follows: Pt(1)–Sb(1) = 2.5854(5), Pt(1)– Sb(2) = 2.6520(5), Re(1)–Sb(1) = 2.7722(5), Re(1)–Re(2) = 3.2742(4), Re(2)–Sb(2) = 2.8025(5), Pt(1)–H(2) = 1.60(9), Re(1)–H(1) = 1.76(1), Re(2)–H(1) = 1.761(10), Pt(1)–P(1) = 2.320(2); Sb(1)–Pt(1)–Sb(2) = 92.017(16), Pt(1)–Sb(1)–Re(1) = 127.094(18), Pt(1)–Sb(2)–Re(2) = 114.513(17).

NMR spectrum [$\delta = -9.9 (1H, {}^{1}J_{195Pt-H} = 912 \text{ Hz}, {}^{2}J_{P-H} = 13 \text{ Hz}), -13.0 (1H, {}^{3}J_{195Pt-H} = 28 \text{ Hz}, {}^{4}J_{P-H} = 10 \text{ Hz})]$ with suitable couplings to the platinum and phosphorus atoms. The Re–Re bond distance in **6** is similar to those found in **3** and **4**: Re(1)–Re(2) = 3.2742(4) Å.

The reaction of **2** with **1** at 68 °C gave compound **4** in 18% yield plus three previously reported compounds: $\text{Re}_2(\text{CO})_{8^-}$ (μ -SbPh_2)₂, ⁹**7** (9% yield); $\text{Re}_2(\text{CO})_7(\text{SbPh}_3)(\mu-\text{H})(\mu-\text{SbPh}_2)$, ⁸**8** (12% yield); and Pt₃(CO)₃(*t*-Bu)₃, ¹¹**9**, 2.8 mg (5% yield). Compound **7** was obtained previously from the thermal decomposition of **1** in the absence of platinum, but that reaction was performed at a much higher temperature (170 °C) than the one reported here.⁹ Compound **8** were obtained previously from the reaction of Re₂(CO)₈(Ph)(SbPh_3)(μ -SbPh₂) with hydrogen at 125 °C.⁵ Compound **9** is readily obtained when solutions of Pt(P-t-Bu₃)₂ are exposed to CO.¹¹



Five products were obtained in low yields when **2** was thermally degraded under nitrogen at 100 °C: $\text{Re}_2(\text{CO})_8(\mu-\text{SbPh}_2)_2$, 7⁹ (6% yield); $\text{RePh}(\text{CO})_4\text{SbPh}_3$, **10**⁸ (4%); $\text{Re}_2-(\text{CO})_8[\text{PtH}(\text{CO})(\text{P-t-Bu}_3)](\mu_3-\text{SbPh})(\mu-\text{SbPh}_2)$, **11**¹⁰ (4%); 5⁷ (4%); $\text{RePh}(\text{CO})_4[\text{PtH}(\text{CO})\text{P}(t-\text{Bu})_3](\mu-\text{SbPh}_2)$, **12** (7%). See Scheme 2. The formation of benzene was confirmed by a ¹H NMR spectrum of the reaction solution.

Of the various products of this reaction, only compound 12 is new. Compound 12 was characterized crystallographically, and an ORTEP diagram of its molecular structure is shown in Figure 6. Compound 12 can be viewed as a CO adduct of 2, and indeed it can be obtained in a similar yield when 2 is treated with CO at room temperature; see below. The formation of 12 in this transformation must have been a result of a CO scavenging process, the latter produced from

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Figure 6. ORTEP diagram of the molecular structure of **12** showing 30% probability thermal ellipsoids. The hydrogen atoms on the ligands are omitted for clarity. Selected interatomic bond distances (Å) and angles (deg) are as follows: Pt(1)-C(7) = 1.863(6), Pt(1)-P(1) = 2.3385(8), Pt1)-Sb(1) = 2.5890(3), Pt(1)-H(1) = 1.48(5), Re(1)-C(1) = 2.229(3), Re(1)-Sb(1) = 2.7451(3), Sb(1)-C(21) 2.147(3), Sb(1)-C(15) = 2.151(3); Pt(1)-Sb(1)-Re(1) = 120.097(9), C(7)-Pt(1)-P(1) = 105.13(16), C(7)-Pt(1)-Sb(1) = 98.62(16), P(1)-Pt(1)-Sb(1) = 155.75(2), C(7)-Pt(1)-H(1) = 172.9(18).

other decomposing molecules of **2**. Compound **12** consists of a Re(CO)₄Ph group and a HPt(P-t-Bu₃)(CO) group held

together by a bridging SbPh2 ligand. There is no metal-metal bond in 12: $Pt \cdots Re = 4.622(1)$ Å. We have recently shown that the hydride and SbPh₂ bridged rhenium-rhenium bond in 8 can be opened by the addition of a hydride ligand.²¹ The Pt-Sb and Re-Sb bond distances in 12 [Pt(1)-Sb(1) =2.5890(3) Å and Re(1)-Sb(1) = 2.7451(3) Å] are slightly longer than those in 2. A CO ligand was added to the platinum atom [Pt(1)-C(7) = 1.863(6) Å], and lies cis to the antimony atom Sb(1). The hydride ligand that bridges the Pt-Re bond in 2 was shifted to a terminal position on the platinum atom in 12 and lies cis to the Sb atom. The hydride ligand was located and refined crystallographically. The Pt-H bond distance is slightly shorter [Pt(1)-H(1) =1.48(5) Å] than the Pt-H bond distance found in 6. The hydride ligand exhibits a high-field resonance shift, $\delta =$ -3.8, with suitable couplings to the phosphorus and platinum atoms, ${}^{1}J_{195Pt-H} = 750$ Hz, ${}^{2}J_{P-H} = 14$ Hz. The bulky P-t-Bu₃ ligand on the platinum atom lies trans to the Sb atom. Compound 11 also contains a HPt(P-t-Bu₃)(CO) group in which the hydride ligand lies cis to the Sb atom and the P-t-Bu₃ ligand lies trans to the Sb atom and has a similar Pt-Sb bond distance, 2.6100(12) Å.⁷ The phenyl

14

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Figure 7. ORTEP diagram of the molecular structure of 14 showing 30% probability thermal ellipsoids. The hydrogen atoms on the ligands are omitted for clarity. Selected interatomic bond distances (Å) and angles (deg) are as follows: Re(1)-Sb(1) = 2.7511(10), Re(1)-Sb(2) = 2.8079(9), Re(2)-Sb(1) = 2.7482(9), Re(2)-Sb(2) = 2.8074(9), Re(3)-Sb(2) = 2.8439(10); Re(2)-Sb(1)-Re(1) = 105.31(3), Re(1)-Sb(2)-Re(2) = 102.26(3), Re(1)-Sb(2)-Re(3) = 117.92(3), Re(2)-Sb(2)-Re(3) = 118.34(3).

group in **12** is σ -bonded to the rhenium atom: Re(1)–C(1) = 2.229(3) Å. Interestingly, the phenyl group in 2 was σ -bonded to the platinum atom. Evidently, the phenyl group was shifted from Pt to Re in the course of the formation of 12. Note: the coproduct 10 also has a phenyl group σ -bonded to a rhenium atom. Compound 10 also contains an SbPh₃ ligand, which indicates that it is possible that the σ -phenyl group in 2 can also be shifted back to the bridging SbPh₂ ligand under these conditions. The formation of 7 suggests that 2 can eliminate a Re(CO)₄SbPh₂ fragment and two of these then combine to form the dimer 7. The addition of a Re(CO)₄SbPh₂ group to **2** accompanied by the elimination of two phenyl groups could account for the formation of 11. Compound 5 was obtained previously from a sequence of reactions of Pt(P-t- Bu_3 and SbPh₃ with 8. It appears that all of the components essential to the formation of 5 are available in the decomposition mixtures of 2^{10}

Seven compounds, 5^{10} (9% yield), 7^9 (26%), 9^{11} (71%), 11^{10} (7%), 12 (8%), 13 (13%), and 14 (18%), were obtained when 2 was allowed to react with CO at room temperature; see Scheme 3. Compound 9 was the major product by far. Compound 13 was obtained previously from the reaction of Re₃(CO)₁₂(μ -H)₃ with Pt(P-t-Bu₃)₂.¹² Compound 14 is new and was fully characterized in this study. The molecular structure of 14 was established by a single-crystal X-ray diffraction analysis, and an ORTEP diagram of it is shown in Figure 7.

Compound 14 contains no platinum at all, but it does contain three rhenium atoms. There are two Re(CO)₄ groups assembled into a Re₂Sb₂ rhombus by a bridging SbPh₂ ligand and a bridging SbPh ligand. The latter contains a pendant Re(CO)₅ group. The Re–Sb bond distances to the bridging SbPh₂ group [Re(1)–Sb(1) = 2.7511(10) Å, Re(1)–Sb(2) = 2.8079(9) Å, and Re(2)–Sb(1) = 2.7482(9) Å] are significantly shorter than those to the SbPh group [Re(1)–Sb(2) = 2.8079(9) Å and Re(2)–Sb(2) = 2.8074(9) Å]. The Re(3)–Sb(2) bond to the Re(CO)₅ group is the longest of all, 2.8439(10) Å. The long Re–Sb bonds to Sb(2) are probably due to the increased sterics produced by the bulky Re(CO)₅ group. A number of compounds containing triply bridging SbPh ligands were obtained from the reactions of 7 and Re₂(CO)₈- $(\mu$ -H)(μ -SbPh₂) with Pt(P-t-Bu₃)₂.^{10,15}

Discussion

In a previous study of the reaction of Pt(P-t-Bu₃)₂ with HOs(CO)₄(SnPh₃), it was found that a Pt(P-t-Bu₃) adduct of HOs(CO)₄(SnPh₃), PtOs(CO)₄SnPh₃(P-t-Bu₃)((μ -H), was formed (see Figure 1), which included the formation of a Pt-Os interaction with a bridging hydrido ligand and a bridging CO ligand. The most important feature of the reaction of 1 with Pt(P-t-Bu₃)₂ is the oxidative-addition of a Sb-C bond of one of the phenyl groups of the SbPh₃ ligand to a Pt(P-t-Bu₃) group formed by the loss of a P-t-Bu₃ ligand, eq 3. A Pt-Re bond was also formed together with a bridging hydrido ligand and a bridging SbPh₂ ligand. The phenyl group that was cleaved from the Sb atom became a σ -bonded ligand on the platinum atom. The cleavage of phenyl groups from PPh₃ and even SbPh₃ has been observed on many previous occasions.^{22,23}



We recently investigated the reaction of $Pt(P-t-Bu_3)_2$ with compound 7 under hydrogen and observed the insertion of

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Pt(P-t-Bu₃) groups into the SbPh bonds of the bridging $SbPh_2$ ligands, e.g., eq 4.¹⁰



The present work shows that the insertion of the Pt(P-t-Bu₃) group into the Sb–C bond of the SbPh₃ ligand of **1** is even more facile and occurs in this case at 25 °C. Interestingly, **2** can react with **1** a second time under more forcing conditions (68 °C) to form the five-membered heterocyclic ring compound **4**, which included a scavenged SbPh₃ ligand from the reaction mixture and the two dirhenium compounds **7** and **8**, eq 3. Although **7** can be obtained directly from **1** at 170 °C, its formation here under milder conditions is undoubtedly due to the ability of the platinum to facilitate cleavage of the phenyl groups from the SbPh₃ ligand. Two other similar five-membered-ring compounds, **3** and **5**, were formed under slightly differing conditions, indicating that

this heterocyclic ring has considerable stability. At 100 °C, compound **2** was degraded and a variety of higher nuclearity species were formed by ligand scrambling, fragmentation, and aggregation of the metal-containing fragments. Several of these degradation products, **5**, **7**, and **11**, were obtained by the reaction of **2** with CO. Compound **12** is a CO adduct of **2** and can also be obtained from **2** by the direct addition of CO, although the yield is not high. Interestingly, the phenyl group was transferred from the platinum atom to the rhenium atom in this process. This transfer may have been facilitated by the addition of the CO ligand to the platinum atom, but the mechanism of this transfer has not been ascertained in this study.

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Supporting Information Available: CIF files for each of the structural analyses are available. This material is available free of charge via the Internet at http://pubs.acs.org.