analogous Mo(V) complexes. The Mo═O distance in $MoOCl_4^-$ and $MoOCl_5^{2-}$ is 1.61 Å[27,28] and that in the *trans*-$MoOX_4(OH_2)^-$ complexes (X = Cl, Br, I) is 1.64 (2) Å, independent of X.[33] These values compare well with the EXAFS-derived Tc═O bond lengths in Table III. Even more importantly, the *cis*- and *trans*-MoCl lengths in $MoOCl_6^{2-}$ (2.39 and 2.59 Å, respectively)[28] are in good agreement with the *cis*- and *trans*-Tc–Cl lengths derived for $TcOCl_5^{2-}$ (2.36 and 2.50 Å). Similarly, the *cis*-Mo–Cl and *cis*-Mo–Br lengths in *trans*-$MoOX_4(H_2O)^-$ (2.364 (5) and 2.53 (2) Å, respectively)[33] are in good agreement with the *cis*-Tc–Cl and *cis*-Tc–Br lengths derived for $TcOX_5^{2-}$ (2.36 and 2.54 Å, respectively).

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Preparation and Characterization of Heterobimetallic Halogen-Bridged Palladium–Platinum Complexes. Crystal and Molecular Structure of $[(PEt_3)ClPd(\mu\text{-}Cl)_2PtCl(PEt_3)]$

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Attempts to prepare and characterize unambiguously heterobimetallic complexes of the type $[(PR_3)ClPd(\mu\text{-}Cl)_2PtCl(PR_3)]$ (R = Et, *n*-Pr, Bu, Ph; $PR_3 = PMe_2Ph$) using infrared, ^{31}P and ^{195}Pt NMR, and mass spectroscopies are described. It is established that, in solution, an equilibrium exists between $[(PR_3)ClPd(\mu\text{-}Cl)_2PtCl(PR_3)]$, $[(PR_3)_2Pd_2Cl_4]$, and $[(PR_3)_2Pt_2Cl_4]$, the latter two species always being in 1:1 molar ratio; this equilibrium is temperature independent but is influenced by excess of either one of the dimers $[(PR_3)_2M_2Cl_4]$ (M = Pt, Pd). The reactions of the heterobimetallic products with $SnCl_2{\cdot}2H_2O$ have been investigated, as well as the bridge-cleavage reactions with various donor ligands, in order to elucidate the chemical behavior of the heterobimetallic dichloro bridge; neutral ligands appear to be distributed equally between Pd and Pt. Crystals of the reaction product, with a composition corresponding to $[(PEt_3)ClPd(\mu\text{-}Cl)_2PtCl(PEt_3)]$ are monoclinic, space group $P2_1/n$, with $a = 7.590$ (2) Å, $b = 12.216$ (1) Å, $c = 12.119$ (1) Å, and $\beta = 101.87$ (1)°. With $Z = 2$ the molecules must lie about inversion centers, and the Pd and Pt atoms are mutually disordered. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations with anisotropic thermal parameters; $R = 0.030$ and $R_w = 0.033$ for 2451 observed reflections. The unique metal atom has slightly distorted square planar geometry with M–P = 2.214 (1), M–Cl (terminal) = 2.275 (1), M–Cl (bridging trans to P) = 2.437 (1), and M–Cl (bridging trans to Cl) = 2.314 (1) Å. The data do not unambiguously identify the solid product but, in combination with the NMR and mass spectroscopic data, do establish conclusively the existence of these heterobimetallic complexes.

Introduction

Halogen-bridged palladium and platinum complexes of the type $[MCl_2(ER_3)]_2$ (M = Pd, Pt; E = P, As, Sb; R = alkyl, aryl) are well-known[1–6] and, from X-ray structural analyses[7,8] usually have symmetrical trans structures. Analogous heterobimetallic complexes containing both palladium and platinum have not been isolated although their existence in solution has been proposed by Masters et al.[9,10] Recently, several heterobimetallic complexes of palladium and platinum containing chelating ligands have been isolated in the solid state.[11–14]

Simple heterobimetallic complexes of the type $[(PR_3)ClPd(\mu\text{-}Cl)_2PtCl(PR_3)]$ are of interest to us in terms of (i) their stereochemistry and bonding, (ii) their behavior in bridge-cleavage reactions with donor ligands, and (iii) their behavior as catalysts or catalyst precursors. We now describe our attempts to prepare the complexes $[(PR_3)ClPd(\mu\text{-}Cl)_2PtCl(PR_3)]$ and to characterize them unambiguously through the determination of the crystal and molecular structure of $[(PEt_3)ClPd(\mu\text{-}Cl)_2PtCl(PEt_3)]$ and through NMR spectroscopic and mass spectroscopic studies.

Results and Discussion

Halogen-bridged heterobimetallic complexes containing both palladium and platinum, of the type $[(PR_3)ClPd(\mu\text{-}Cl)_2PtCl(PR_3)]$ with R = Et, Pr, *n*-Bu, or Ph or $PR_3 = PMe_2Ph$, can apparently be easily prepared by the reactions of *trans*-$(PR_3)_2PtCl_2$ with palladium(II) chloride, or $(PR_3)_2\,PdCl_2$ with platinum(II) chloride, in refluxing xylene in an inert atmosphere. The resulting products are orange, crystalline solids readily soluble in dichloromethane, chloroform, benzene, toluene, and xylene (except the triphenylphosphine complex, which is sparingly soluble in these solvents). Analytical and physical data are given in Table I.

This synthesis might obviously be extended to systems such as *trans*-$[(PtHCl(PEt_3)_2]$ with $PdCl_2$, in which, if the analogous reaction occurred, a heterobimetallic species containing both hydrido and chlorobridging might be obtained. Unfortunately,

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Table I. Analytical and Physical Data for Heterobimetallic Complexes

complex	color [cryst solvent]	mp, °C	anal. found (calcd)		
			C	H	Cl
$[(PEt_3)_2PtPdCl_4]^a$	orange $[CH_2Cl_2]$	217–219^d	21.04 (21.21)	4.74 (4.45)	21.02 (20.87)
$[(PPr_3)_2PtPdCl_4]^a$	orange ($CHCl_3$/hexane)	175–178^d	28.36 (28.30)	5.61 (5.54)	18.71 (18.57)
$[(PPr_3)_2PtPdCl_4]^b$	orange ($CHCl_3$/hexane)		28.22 (28.30)	5.68 (5.54)	18.53 (18.57)
$[(PBu_3)_2PtPdCl_4]^b$	orange-red ($CHCl_3$/hexane)	140–142	34.07 (33.99)	6.62 (6.42)	16.50 (16.72)
$[(PPh_3)_2PtPdCl_4]^b$	orange^c	248–258 dec	44.29 (44.67)	3.22 3.12	14.26 (14.65)
$[(PPhMe_2)_2PtPdCl_4]^b$	orange ($CHCl_3$/hexane)	215–217 dec	26.76 (26.71)	3.01 (3.08)	19.68 (19.71)

[a] From $PdCl_2$. [b] From $PtCl_2$. [c] Extracted from dichloromethane and used as such without further recrystallization. [d] Decompose with melting.

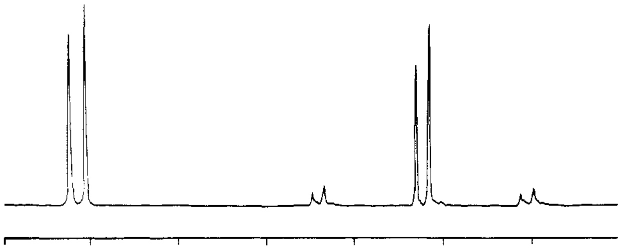

Figure 1. ^{31}P NMR spectrum of $[(P\text{-}n\text{-}Bu_3)ClPd(\mu\text{-}Cl)_2PtCl(P\text{-}n\text{-}Bu_3)]$ in $CDCl_3$.

Table II. Infrared Absorption Frequencies (cm^{-1}) for the Binuclear Complexes $[MM'(PR_3)_2Cl_4]$ (M and M' = Pt or Pd or Both) in the 400–200 cm^{-1} Region

PR_3	M = M' = Pd^a	M = Pd, M' = Pt^b	M = M' = Pt^a
PEt_3	376 356 t 329 301 b 260 sh 257 249 b	352, tM 348, tM' 338 sh 322, bM' 295, bM 258, bM' 250 sh, bM 242 sh	384 351 t 344 sh 327 b 315 sh 265 b 253 sh
P-*n*-Pr_3	356 t 304 sh 299 b 253 b 235 sh	355, tM 345 sh, tM' 322, bM' 318 sh 312 sh 298, bM 255, bM, M' 245 sh	377 356 t 348 sh 323 b 315 sh 257 b
P-*n*-Bu_3	...	362 sh, tM 347, tM' 340 sh 330 sh 317, bM' 292, bM 249, bM, M' 240 sh	...
PPh_3	359 t 297 b 275 260 b 253 sh 231	360, tM 358 sh, tM' 345 320, bM' 314 300, bM' 265 sh 260, bM' 250 sh, bM	398 359 t 352 sh 326 sh 320 b 312 sh 276 sh 268 sh 260 b 254 sh 236 210
$PPhMe_2$		352, tM 350 sh, tM' 345 sh 323, bM' 317, bM' 288 250, bM' 245, bM 225	

[a] From ref 13. [b] ±5 cm^{-1}. Key: t = terminal; b = bridging; sh = shoulder.

when such a mixture was treated under reflux in toluene or xylene, decomposition occurred, with a metallic precipitate and *cis*- and *trans*-$(PEt_3)_2PtCl_2$ being formed.

Infrared absorption frequencies for these heterobimetallic products in the 400–200 cm^{-1} region are listed in Table II, together with those for $[PdCl_2(PR_3)]_2$ and $[PtCl_2(PR_3)]_2$, from which, by comparison, assignments for the various M–Cl vibrations have been made. In the heterobimetallic complexes, the following vibrations could be expected: (i) ν(Pd–Cl) (terminal); (ii) ν(Pt–Cl) (terminal); (iii) ν(Pd–Cl) (bridging trans to Cl); (iv) ν(Pd–Cl) bridging (trans to PR_3); (v) ν(Pt–Cl) (bridging trans to Cl); (vi) ν(Pt–Cl) (bridging trans to PR_3). In $[M(PR_3)Cl_2]_2$ infrared absorption arising from stretching vibrations of terminal M–Cl bonds occurs at ca. 355 cm^{-1} regardless of whether M is Pd or Pt.[15-17] For $[(PEt_3)ClPd(\mu\text{-}Cl)_2PtCl(PEt_3)]$, we observe (Table II) two infrared bands at 352 and 348 cm^{-1}, which can therefore be assigned to vibrations associated with terminal Pd–Cl and Pt–Cl stretching vibrations. However, for the analogous P-*n*-Pr_3, P-*n*-Bu_3, PPh_3, and PMe_2Ph complexes, only one band with a much less intense shoulder is observed in this region and can be assigned similarly.

In earlier studies of $[MCl_2(PR_3)]_2$, infrared absorptions associated with ν(M–Cl) (bridging trans to Cl) have been observed at ~300 cm^{-1} (M = Pd) and ~325 cm^{-1} (M = Pt), while those arising from ν(M–Cl) (bridging trans to phosphine) are at lower frequency (~250 cm^{-1} for Pd and ~260 cm^{-1} for Pt). These latter absorptions have also been found to be sensitive to the specific phosphine ligand.[15-17] Accordingly, in the infrared spectra of the heterobimetallic complexes, bands observed at ~300 and ~320 cm^{-1} are associated with ν(M–Cl) (bridging trans to Cl), while bands at ~255 cm^{-1}, which generally displayed one or more shoulders, are assigned to ν(M–Cl) (bridging trans to phosphine).

The ^{31}P NMR spectral data of these products are given in Table III. In each case, four phosphorus resonances are observed, only two of which show coupling to ^{195}Pt but with different $^1J(PtP)$ values, while the remaining two signals are sharp singlets without satellites (Figure 1). These spectra were unchanged over a period of days. The former two resonances with ^{195}Pt satellites are assigned to phosphorus nuclei bound to platinum, and the latter two singlets to phosphorus bound to palladium. We first con-

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Table III. ^{31}P NMR Spectral Data for $[(PR_3)_2MM'Cl_4]$ Complexes in $CDCl_3$ at 25 °C

	$[(PR_3)PdCl(\mu\text{-}Cl)_2PtCl(PR_3)]$				$[(PR_3)PtCl_2]_2$	
phosphine	Pd δ(P)	Pt δ(P)	$^1J(^{195}Pt-^{31}P)$, Hz	$[(PR_3)PdCl_2]_2$ δ(P)	δ(P)	$^1J(^{195}Pt-^{31}P)$, Hz
PEt_3	50.4	9.6	3864	48.6	11.0	3842
P-*n*-Pr_3	41.4	1.0	3838	39.6	2.4	3819
P-*n*-Bu_3	42.3	1.6	3842	40.5	3.0	3818
$PPhMe_2$	15.3	−18.8	3948	16.9	−17.6	3926

sidered that, as has been reported[18] for $[(PPh_3)PtCl_2]_2$, two isomers, cis and trans, might exist in solution in equilibrium, with each isomer showing a different Pt–P coupling constant and with the two isomers being present in an approximate 4:5 ratio.

However, comparison of the observed ^{31}P NMR spectrum with those of $[(PEt_3)PtCl_2]_2$ and $[(PEt_3)PdCl_2]_2$ showed that two of the observed peaks (one with ^{195}Pt satellites and one without) were attributable to the latter two compounds, leaving the expected two resonances, one of which shows Pt–P coupling, to be assigned to $[(PEt_3)ClPd(\mu\text{-}Cl)_2PtCl(PEt_3)]$. This suggests that the heterobimetallic complex disproportionates readily in solution to establish the equilibrium

$$2[(PEt_3)ClPd(\mu\text{-}Cl)_2PtCl(PEt_3)] \rightleftharpoons [(PEt_3)PdCl_2]_2 + [(PEt_3)PtCl_2]_2$$

This was confirmed by mixing CH_2Cl_2 or $CHCl_3$ solutions containing equimolar amounts of $[(PEt_3)PdCl_2]_2$ and $[(PEt_3)PtCl_2]_2$ at room temperature, to generate a ^{31}P NMR spectrum identical with that observed with a solution of the heterobimetallic complex. In both cases, therefore, the three species described by the above equilibrium appear to be present in the 2.2:1:1 ratio. When solutions of $[(PEt_3)PdCl_2]_2$ and $[(PEt_3)PtCl_2]_2$ are mixed in a 1:2 molar ratio [Pt:Pd = 1:2 or vice versa], the ^{31}P NMR spectrum indicates that the ratio of the resulting heterobimetallic complex to the reactant not in excess is 3:1. In similar reactions of 1:5 or 1:10 stoichiometry (Pt:Pd = 1:5 or 1:10 or vice versa) only two species were observed in solution, namely $[(PEt_3)ClPd(\mu\text{-}Cl)_2PtCl(PEt_3)]$ and $[(PEt_3)MCl_2]_2$ (M = Pd, Pt).

Interestingly, when the mercapto-bridged (stable bridge) dimers, *cis*-$[(PPr_3)PdCl(\mu\text{-}SEt)]_2$ and *cis*-$[(PPr_3)PtCl(\mu\text{-}SEt)]_2$, were mixed in 1:1 stoichiometry in $CDCl_3$ at room temperature, no heterobimetallic complex of the type $[(PPr_3)ClPd(\mu\text{-}SEt)_2PtCl(PPr_3)]$ appeared to be formed, as the ^{31}P NMR spectrum, which was unchanged over a period of days, displayed only two resonances, one for the Pd dimer and the other for the Pt dimer with $^1J(^{195}Pt-^{31}P)$ = 3168 Hz. If the exchange proceeds via a bimolecular process involving the interaction of two dimers, as suggested by earlier workers,[9,10] one would expect the mercapto-bridged heterobimetallic complexes in the above solution. Since such a complex does not exist in a freshly prepared solution of a mixture of mercapto-bridged Pd and Pt dimers, it seems unlikely that a mechanism involving direct interaction of two dimers is responsible for the exchange reaction:

$$[(PR_3)PdCl_2]_2 + [(PR_3)PtCl_2]_2 \rightleftharpoons [(PR_3)ClPd(\mu\text{-}Cl)_2PtCl(PR_3)]$$

Masters et al.[9,10] have observed a temperature dependence of the ^{31}P NMR spectrum of an equimolar mixture of $[(PBu_3)PdCl_2]_2$ and $[(PBu_3)PtCl_2]_2$, and at −16 °C resolution of the palladium-bound signal was possible. In contrast, in our studies, we have observed that in toluene-d_8 the ^{31}P NMR spectrum of $[(PBu_3)ClPd(\mu\text{-}Cl)_2PtCl(PBu_3)]$ was unchanged over the temperature range −70 to +80 °C, other than some small temperature dependence of the chemical shift values. Thus, the shift for palladium-bound phosphorus is deshielded from δ 42.3 and 40.2 at −70 °C to δ 35.0 and 33.4 at 80 °C, while for platinum-bound phosphorus the resonances are increasingly shielded from −70 to +5 °C (δ 3.4 and 1.7 at −70 °C and δ 2.6 and 1.3 at +5 °C) and then show little change up to 80 °C (δ 2.7 and −3.9).

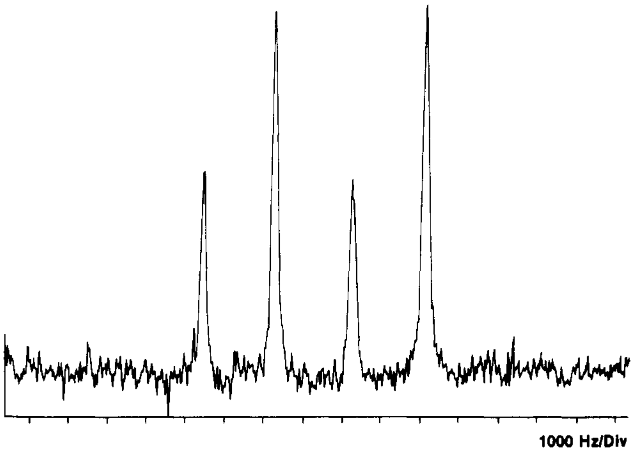

Figure 2. ^{195}Pt NMR spectrum of $[(P\text{-}n\text{-}Bu_3)ClPd(\mu\text{-}Cl)_2PtCl(P\text{-}n\text{-}Bu_3)]$ in $CDCl_3$ with Na_2PtCl_4 as reference.

Also, at temperatures of −40 °C or lower, the satellites due to ^{195}Pt coupling are broad and poorly resolved but become sharp and well-defined above −40 °C, perhaps indicative of some type of exchange process. Surprisingly, therefore, the above equilibrium appears to be temperature independent.

In the ^{195}Pt NMR spectrum, two doublets with different ^{31}P–^{195}Pt coupling constants were observed, suggesting the presence of two platinum-containing species in solution (Figure 2). The integral ratio for the two is approximately 3:7, the less abundant being $[(PR_3)_2Pt_2Cl_4]$. Thus, the ^{195}Pt NMR chemical shifts for the complexes are as follows: $[(PPr_3)_2PtPdCl_4]$, δ(Pt) = −1786.9 (^1J)($^{195}Pt-^{31}P$) = 3834 Hz); $[(PPr_3)_2Pt_2Cl_4]$, δ −1764.6 ($^1J(^{195}Pt-^{31}P)$ = 3819 Hz); $[(PBu_3)_2PtPdCl_4]$, δ(Pt) = −1796.0 ($^1J(^{195}Pt-^{31}P)$ = 3857 Hz); $[(PBu_3)_2Pt_2Cl_4]$, δ −1774.4 ($^1J(^{195}Pt-^{31}P)$ = 3807 Hz). The ^{31}P and ^{195}Pt NMR spectra of $[(PBu_3)ClPd(\mu\text{-}Cl)_2PtCl(PBu_3)]$ in $CDCl_3$ are displayed in Figures 1 and 2.

We have also investigated the reactions of the heterobimetallic complexes with $SnCl_2{\cdot}2H_2O$, using ^{31}P NMR spectroscopy in the hope that this would throw further light on the equilibria in solution. We have reported on similar studies with $[(PR_3)_2Pt_2(\mu\text{-}Cl)_2Cl_2]$ recently.[19,20] The ^{31}P NMR spectra were recorded at room temperature after the addition of 1.0, 2.0, 5.0, and 10.0 equiv of $SnCl_2{\cdot}2H_2O$ to the dichloromethane solutions of $[(PBu_3)ClPd(\mu\text{-}Cl)_2PtCl(PBu_3)]$, with the products being identified where possible by comparison of the observed chemical shifts and coupling constants $^1J(^{195}Pt-^{31}P)$ with those previously reported for similar complexes.[19,20] The reactions in 1:1 and 1:2 stoichiometry appeared to be complex; the addition of 1 equiv of $SnCl_2{\cdot}2H_2O$ to the solution of $[(PBu_3)ClPd(\mu\text{-}Cl)_2PtCl(PBu_3)]$ gave five phosphorus-containing species: (A) identified as $[(PBu_3)(SnCl_3)Pd(\mu\text{-}Cl)_2Pt(SnCl_3)(PBu_3)]$ (δ(Pd–P) = 35.06, δ(Pt–P) = 0.04, $^1J(^{195}Pt-^{31}P)$ = 3433 Hz); (B) contained phosphine bound only to Pd (δ(Pd–P) = 34.07), with (A) and (B) each comprising 40% of the product mixture; (C) identified as the dimeric palladium complex $[(PBu_3)_2Pd_2Cl_2(\mu\text{-}Cl)_2]$ (δ(P) = 40.1); (D) tentatively identified as $[(PBu_3)ClPd(\mu\text{-}Cl)_2Pt(SnCl_3)(PBu_3)]$ (δ(Pd–P) = 36.64, δ(Pt–P) = 2.60, $^1J(^{195}Pt-^{31}P)$ = 3600 Hz); (E)

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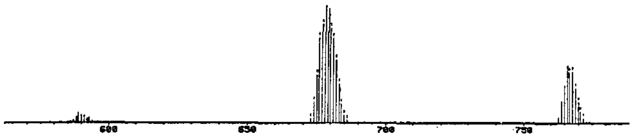

Figure 3. FD mass spectrum of $[(PEt_3)ClPd(\mu\text{-}Cl)_2PtCl(PEt_3)]$ at 70 °C.

tentatively thought to be $[(PBu_3)(SnCl_3)Pd(\mu\text{-}Cl)_2PtCl(PBu_3)]$ (δ(Pd–P) = 38.6, δ(Pt–P) = −1.1, $^1J(^{195}Pt–^{31}P)$ = 3660 Hz). The reaction carried out with a 1:2 stoichiometry gave all the above products, but the percentage of the reaction product mixture made of (D) and (E) was much reduced. Reactions in 1:5 or 1:10 (PdPt/Sn) stoichiometry gave yellow solutions whose ^{31}P NMR spectra were identical, indicating that reaction was complete. Only (A) and (B) in an approximate ratio of 3:2 were then observed in the reaction solution, with no trace of (C), (D), or (E).

The mass spectra of $[(PEt_3)PdCl_2]_2$, $[(PEt_3)PtCl_2]_2$, and $[(PEt_3)ClPd(\mu\text{-}Cl)_2PtCl(PEt_3)]$ and the mixture of $[(PEt_2)PdCl_2]_2$ and $[(PEt_3)PtCl_2]_2$ were recorded at 225 °C. At this temperature the palladium dimer did not show any reasonably defined isotopic pattern, while the $[(PEt_3)PtCl_2]_2$ dimer displayed an intense peak at m/e 768 with an isotopic pattern corresponding to that calculated. The heterobimetallic dimer $[(PEt_3)ClPd(\mu\text{-}Cl)_2PtCl(PEt_3)]$ displayed two peaks in the region m/e 660–780; one at m/e 681 showed an isotope pattern corresponding to the heterobimetallic dimer and the other at m/e 768 an isotopic pattern corresponding to the dimer $[(PEt_3)PtCl_2]_2$. In fact, the total spectrum thus obtained for this heterobimetallic dimer is identical with that obtained from an equimolar mixture of $[(PEt_3)PdCl_2]_2$ and $[(PEt_3)PtCl_2]_2$. Since all of these dimers melt with decomposition in the range 217–230 °C, it appears that such decomposition occurs in the mass spectrometer (~225 °C) prior to electron impact. Accordingly, the mass spectrum of $[(PEt_3)ClPd(\mu\text{-}Cl)_2PtCl(PEt_3)]$ was then recorded at 70 °C by the field desorption method in chloroform solution and is shown in Figure 3. The spectrum displayed an intense molecular ion peak for the heterobimetallic dimer along with less intense molecular ion peaks for $[(PEt_3)PdCl_2]_2$ and $[(PEt_3)PtCl_2]_2$. The intensities for the latter two complexes differ considerably from each other, which could be due to different ionization efficiencies of two dimers. Therefore, while the mass spectroscopic data confirm the existence of the heterobimetallic species, they do not provide evidence as to whether the original solid consists of the pure complex that then disproportionates at ~225 °C or alternatively consists of the heterobimetallic complex together with equimolar amounts of $[(PR_3)_2Pt_2Cl_4]$ and $[(PR_3)_2Pd_2Cl_4]$. Solid-state ^{195}Pt NMR parameters might show such a differentiation; however, we have found that the line widths are too great (~300 kHz) to distinguish between the PdPt and Pt_2 species.

A characteristic reaction of the halogen-bridged binuclear complexes $[M(PR_3)Cl_2]_2$ is that with neutral donor ligands that symmetrically cleave the halogen bridge. It was therefore of interest to examine such reactions of their heterobimetallic analogues with donor ligands of different trans influence. Also, the geometry of the products would be of further interest, in view of the different tendencies of Pd and Pt to form cis or trans complexes.[5,21] ^{31}P NMR spectroscopy was employed to follow the course of reactions, as well as to determine the geometry of the products. In the cleavage reaction of $[(P\text{-}n\text{-}Pr_3)ClPd(\mu\text{-}Cl)_2PtCl(P\text{-}n\text{-}Pr_3)]$ with carbon monoxide, the ^{31}P NMR spectrum of the deuteriochloroform solution of the reaction mixture showed 100% conversion to mononuclear products, in which each metal atom contains one phosphine ligand (δ(PdP) = 34.3, δ(PtP) = 8.8, ^1J(PtP) = 2778 hz). The magnitude of ^1J defines a cis geometry for the platinum carbonyl product.[22] A similar cleavage reaction with pyridine in $CDCl_3$ yields palladium and platinum mononuclear complexes, each having one phosphine ligand. The ^{31}P NMR spectrum shows two phosphorus resonances at δ 22.0 (P bound to Pd) and δ −13.1 with ^1J(PtP) = 3335 Hz (P bound to Pt). The latter species is assigned a trans geometry on the basis of the ^1J value. Pidcock et al.[23] prepared $(P\text{-}n\text{-}Bu_3)(py)PtCl_2$ by the bridge-cleavage reaction of $[(P\text{-}n\text{-}Bu_3)PtCl_2]_2$ with pyridine and assigned a trans geometry to this product. The observed large coupling constant of 3360 Hz was attributed to an increase in covalency of the Pt–P bond due to the greater electronegativity of nitrogen.[23]

The similar bridge-cleavage reaction of $[(P\text{-}n\text{-}Pr_3)ClPd(\mu\text{-}Cl)_2PtCl(P\text{-}n\text{-}Pr_3)]$ with triphenylarsine in $CDCl_3$ solution gives three products, $[(P\text{-}n\text{-}Pr_3)(AsPh_3)PdCl_2]$ and *cis*- and *trans*-$[(P\text{-}n\text{-}Pr_3)(AsPh_3)PtCl_2]$. After a reaction time of 1 h, the ^{31}P NMR spectrum shows three resonances, one a singlet, with no ^{195}Pt coupling, at δ 16.1 (P bound to Pd) and others at δ −1.6 with ^1J(PtP) = 3050 Hz and at δ 8.1 with ^1J(PtP) = 3347 Hz. The cleavage reaction of $[(P\text{-}n\text{-}Pr_3)ClPd(\mu\text{-}Cl)_2PtCl(P\text{-}n\text{-}Pr_3)]$ with tri-*n*-propylphosphine also gives three products, $[(P\text{-}n\text{-}Pr_3)_2PdCl_2]$ and *cis*- and *trans*-$[(P\text{-}n\text{-}Pr_3)_2PtCl_2]$, as three phosphorus resonances have been observed in the ^{31}P NMR spectrum of the reaction mixture after 1h. These three resonances appeared at δ 9.8 for palladium-bound phosphorus and δ 4.4 ($^1J(^{195}Pt–^{31}P)$ = 2379.9 Hz) and δ 0.7 (3508.8 Hz) of cis and trans isomers of platinum-bound phosphorus. Reaction with triphenylphosphine yields $[(PPr_3)(PPh_3)PdCl_2]$ (δ 13.9, 12.7) and mainly *cis*-$[(P\text{-}n\text{-}Pr_3)(PPh_3)PtCl_2]$ (δ 8.5, ^1J = 3822 Hz; δ −7.3, ^1J = 3372 Hz); the cleavage reactions of $[(PR_3)PtCl_2]_2$ with triphenylphosphine give trans products[23-25] that can be isomerized to cis isomers in the presence of catalytic amounts of PPh_3. Thus, the formation of the cis isomer in the cleavage reaction of $[(P\text{-}n\text{-}Pr_3)ClPd(\mu\text{-}Cl)_2PtCl(P\text{-}n\text{-}Pr_3)]$ with PPh_3 may be due to the isomerization of the initially formed trans product to cis isomer in the presence of catalytic amounts of free PPh_3.

Such bridge-cleavage reactions with neutral donor ligands appear to occur symmetrically, uninfluenced by the heterobimetallic nature of the complex, by the greater tendency of palladium than platinum to form trans products, or by differences in the trans influence of the incoming ligand.

The crystal structure of $[(PEt_3)ClPd(\mu\text{-}Cl)_2PtCl(PEt_3)]$ (Figure 4) consists of discrete molecules of the binuclear complex separated by normal van der Waals distances. The molecule (Figure 4; Table IV) lies about an inversion center that demands equal disorder of Pd and Pt atoms; the disordered PdPt atom is shown by M in Figure 5. The result of our analysis shows that the disorder has no large effect on the remaining atoms of the molecule; in particular, the PEt_3 moiety has close to normal dimensions and the vibration parameters show no signs of undue disorder, presumably this is helped by the fact that Pd–P and Pt–P bond lengths (2.310–2.388 (6)[26] and 2.202–2.282 (3) Å[27]) do not differ greatly. Our observed M–P distance is 2.214 (1) Å.

The geometry around the metal atom is slightly distorted square planar (Table IV). Because of the disorder of the Pd and Pt atoms we cannot distinguish between Pd–Cl and Pt–Cl dimensions nor between Pd–P and Pt–P dimensions. The M–Cl (terminal) bond length, 2.275 (1) Å, is shorter, as expected, than the M–Cl (bridging) distances (2.314 (1), 2.437 (1) Å), which in turn show a marked trans effect (the larger distance being trans to P).

The M–P–C(1)–C(2) moiety is maximally extended (torsion angles Cl(2)–M–P–Cl(1) = −179.7 (5) and M–P–C(1)–C(2) = −177.9 (5)°), and this conformation results in the hydrogens on C(1) being adjacent to $Cl(1)^1$, with Cl...H = 2.89 and 2.99 Å, close to the sum of the van der Waals radii (2.90 Å).[28] This is

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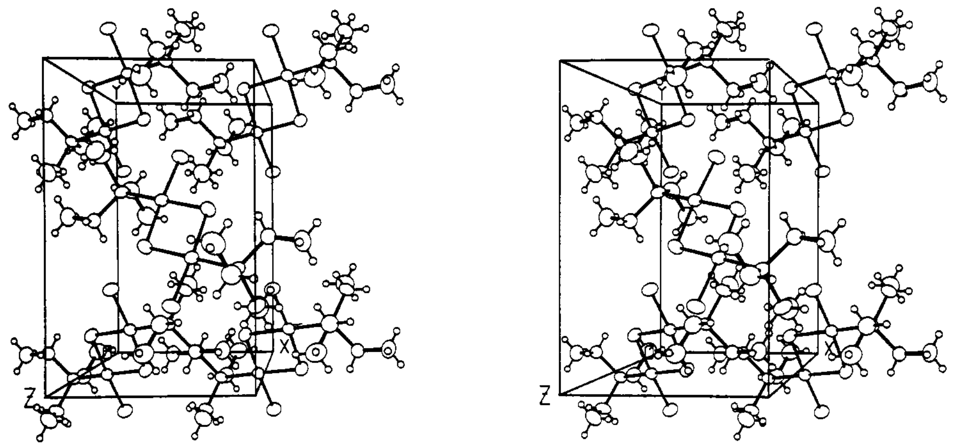

Figure 4. Stereoview of the crystal structure of [$(PEt_3)ClPd(\mu\text{-}Cl)_2PtCl(PEt_3)$].

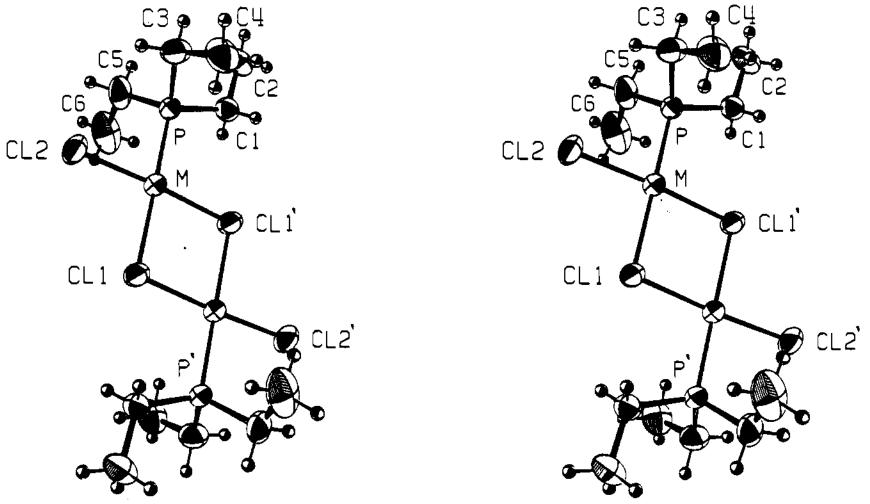

Figure 5. Stereoview of a molecule of the centrosymmetric complex. M represents the disordered PdPt atom.

achieved by a slight opening of the P–M–Cl(1)^1 angle to 95.6 (1)° with a concomitant reduction of the P–M–Cl(2) angle to 88.2 (1)°.

As is commonly found in trialkylphosphine complexes,[29–31] the M–P–C and P–C–C angles (112.1–112.5 (1) and 114.5–116.0 (4)°, respectively) are greater than the C–P–C angles (105.7–106.8 (3)°), which are all less than tetrahedral. The remaining dimensions in the phosphine moiety (mean P–C = 1.806 (5) and C–C = 1.507 (8) Å) are normal and are in accord with accepted values.

Thus, while ^{31}P NMR solution spectroscopic, mass spectroscopic, and chemical data all indicate that the equilibrium

$$2[(PR_3)ClPd(\mu\text{-}Cl)_2PtCl(PR_3)] \rightleftharpoons [(PR_3)PdCl_2]_2 + [(PR_3)PtCl_2]_2$$

occurs in solution, the precise nature of the solid complex is still unclear. All available data, including the crystal structure determination, are consistent with any one of the following compositions: (a) the solid product is the pure heterobimetallic complex [$(PR_3)ClPd(\mu\text{-}Cl)_2PtCl(PR_3)$]; (b) the solid product is a 1:1 mixture of [$PR_3PdCl_2]_2$ and [$PR_3PtCl_2]_2$; which must cocrystallize with complete disorder; (c) the solid product consists of the heterobimetallic complex *plus* a 1:1 mixture of [$PR_3PdCl_2]_2$ and [$PR_3PtCl_2]_2$. In view of the mass spectroscopic data that unambiguously establish the existence of the heterobimetallic complex, we reject (b) as a possibility, but all of the experimental evidence does not allow any differentiation between (a) and (c). We have been unable, to date, to devise an experiment that will provide such an unambiguous differentiation.

Experimental Section

Phosphine ligands were obtained from Strem Chemicals, and all manipulations involving them were performed under a nitrogen atmosphere. Spectrograde solvents were used in all experiments.

^{31}P NMR spectra were obtained on a Bruker WH-400 instrument operating in the Fourier transform mode at 161.98 MHz. Spectra were recorded in $CDCl_3$ solution unless otherwise stated, and ^{31}P chemical shifts were measured relative to external H_3PO_4, more positive values representing deshielding. ^{195}Pt NMR spectra were recorded on a Bruker WH-400 instrument operating in the Fourier transform mode at 85.88 MHz. Spectra were recorded in $CDCl_3$ solutions, and chemical shifts are relative to Na_2PtCl_4. Infrared spectra were obtained on a Perkin-Elmer 180 spectrometer using Nujol walls between CsI plates. Mass spectra were recorded on CH7 Varian Mat spectrometer. The mass spectrum of [$(PEt_3)ClPd(\mu\text{-}Cl)_2PtCl(PEt_3)$] was also recorded on Mat CH-5 double-focusing mass spectrometer by field desorption method at 70 °C in chloroform. Elemental analyses were performed by Guelph Chemical Laboratories Ltd.

[$(PR_3)_2PdCl_2$] and *trans*-[$(PR_3)_2PtCl_2$] were prepared by the literature methods.[32–34] Mercapto-bridged complexes [$(P\text{-}n\text{-}Rr_3)PdCl(\mu\text{-}SEt)]_2$ and [$(P\text{-}n\text{-}Pr_3)PtCl(\mu\text{-}SEt)]_2$ were prepared by the method of Chatt and Hart.[35]

The new heterobimetallic complexes were all prepared similarly, a typical preparation being as follows:

Preparation of [$(P\text{-}n\text{-}Pr_3)ClPd(\mu\text{-}Cl)_2PtCl(P\text{-}n\text{-}Pr_3)$]. [$(P\text{-}n\text{-}Pr_3)_2PdCl_2$] (0.213 g) and $PtCl_2$ (0.124 g) (or *trans*-[$(P\text{-}n\text{-}Pr_3)_2PtCl_2$] (0.379 g) and $PdCl_2$ (0.126 g)) were finely ground together in a mortar

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Table IV. Interatomic Distances (Å) and Angles (deg) with Esd's in Parentheses for $[(PEt_3)MCl_2]_2$

(a) Distances[a]

M-Cl(1)	2.437 (1)	P-C(3)	1.798 (5)
M-Cl(1)$^{\mathrm{I}}$	2.314 (1)	P-C(5)	1.806 (5)
M-Cl(2)	2.275 (1)	C(1)-C(2)	1.510 (6)
M-P	2.214 (1)	C(3)-C(4)	1.538 (9)
P-C(1)	1.815 (5)	C(5)-C(6)	1.473 (9)

(b) Angles

Cl(1)-M-Cl(1)$^{\mathrm{I}}$	84.3 (1)	M-P-C(1)	112.8 (1)
Cl(1)-M-Cl(2)	92.0 (1)	M-P-C(3)	112.7 (2)
Cl(1)-M-P	178.8 (1)	M-P-C(5)	112.1 (2)
Cl(1)$^{\mathrm{I}}$-M-Cl(2)	176.1 (1)	C(1)-P-C(3)	106.2 (2)
Cl(1)$^{\mathrm{I}}$-M-P	95.6 (1)	C(1)-P-C(5)	106.8 (3)
Cl(2)-M-P	88.2 (1)	C(3)-P-C(5)	105.7 (3)
M-Cl(1)-M$^{\mathrm{I}}$	95.7 (1)	P-C(1)-C(2)	116.0 (4)
		P-C(3)-C(4)	114.5 (4)
		P-C(5)-C(6)	115.0 (4)

(c) Torsion Angles

Cl(1)M-PC(1)	−82.5 (2)	MP-C(1)C(2)	−177.9 (5)
Cl(1)M-PC(3)	157.3 (3)	MP-C(3)C(4)	56.8 (6)
Cl(1)M-PC(5)	38.0 (3)	MP-C(5)C(6)	−47.7 (6)
Cl(2)M-PC(1)	−179.7 (2)	Cl(1)$^{\mathrm{I}}$-M-PC(1)	1.2 (2)
Cl(2)M-PC(3)	60.0 (2)	Cl(1)$^{\mathrm{I}}$-M-PC(3)	−119.0 (3)
Cl(2)M-PC(5)	−59.1 (3)	Cl(1)$^{\mathrm{I}}$-M-PC(5)	121.9 (3)

(d) Deviations (Å) of Atoms from the Least-Squares Plane for M, P, Cl(1), Cl(1)$^{\mathrm{I}}$, and Cl(2)

atom	dev, Å	atom	dev, Å
M	0.001	Cl(1)$^{\mathrm{I}}$	0.022
P	−0.023	Cl(2)	0.022
Cl(1)	−0.022		

(e) Intramolecular Nonbonded Distances

M···H(62)	3.11	Cl(2)···H(31)	2.99
Cl(1)$^{\mathrm{I}}$···H(11)	2.99	Cl(2)···H(52)	3.03
Cl(1)$^{\mathrm{I}}$···H(12)	2.89		

[a] The superscript I refers to equivalent position $-x, -y, -z$.

and transferred to a 20-mL flask, and then about 5 mL of xylene was added. The mixture was heated under reflux with stirring under a nitrogen atmosphere until all of the metal dichloride was dissolved at which point reaction is complete (ca. 10 min of refluxing). After the mixture has been cooled, solvent is pumped off under vacuum and the residue is washed well with hexane and extracted with chloroform. The extract is passed over a small Florisil column to remove any unreacted dichloride and decomposition products, after which the volume is reduced to about 10 mL by passage of a stream of air. Hexane (~10 mL) is added from which slow crystallization occurs; yield 0.24 g (0.2 g from $PdCl_2$). Pertinent analytical and other data are given in Table I.

Reactions of $[(PBu_3)ClPd(\mu\text{-}Cl)_2PtCl(PBu_3)]$ with $SnCl_2 \cdot 2H_2O$ were performed by mixing the stoichiometric amounts of $SnCl_2 \cdot 2H_2O$ with the stirring solution of the dimer (~50 mg) in CH_2Cl_2 in a 10-mL flask, and the reactants were stirred for about 30 min. The sample was then filtered into an NMR tube and examined spectroscopically.

Cleavage Reactions of $[(P\text{-}n\text{-}Pr_3)ClPd(\mu\text{-}Cl)_2PtCl(P\text{-}n\text{-}Pr_3)]$. (i) Carbon Monoxide. Carbon monoxide was bubbled through a $CDCl_3$ solution of the binuclear complex (0.075 g) for 1 h, and the ^{31}P NMR spectrum of the reaction mixture was then examined. Small amounts of a metallic precipitate were also formed during this reaction.

(ii) Pyridine. A solution of pyridine (0.031 g) in $CDCl_3$ was added with stirring to a $CDCl_3$ solution of the binuclear complex (0.109 g), yielding a yellow solution that was examined spectroscopically after 1 h.

(iii) Triphenylphosphine and Triphenylarsine. At stoichiometric amount of the ligand was added to a $CDCl_3$ solution of the binuclear complex (~75 mg), yielding a cream-colored solution that was examined spectroscopically.

Crystal Data for $[(PEt_3)ClPd(\mu\text{-}Cl)_2PtCl(PEt_3)]$: $C_{12}H_{30}Cl_4P_2PdPt$, $M_r = 679.6$, monoclinic, $a = 7.590$ (2) Å, $b = 12.216$ (1) Å, $c = 12.119$ (1) Å, $\beta = 101.87$ (1)°, $V = 0.071069$ Å, μ(Mo Kα) = 8.10 cm^{-1}; space group $P2_1/n$ uniquely from the systematic absences (h0l absent if $h + l = 2n$ 1; 0k0 absent if $k = 2n + 1$).

Structure Determination. Accurate unit cell constants and the crystal orientation matrix were determined on an Enraf-Nonius CAD4 diffractometer by a least-squares treatment of the setting angles of 25 relections with θ in the range 10–20°. Intensity data were collected by the ω–2θ scan method using monochromatized Mo Kα radiation in the range $2 < \theta < 30°$. The intensities of three reflections, chosen as standards, were monitored at regular intervals and showed no reduction in intensity. Intensities of 3191 unique reflections were measured, of which 2451 had $I > 3\sigma(I)$ and were used in structure solution and refinement. Data were corrected for Lorentz and polarization factors and for absorption. Maximum and minimum values of the transmission coefficients are 0.3185 and 0.2574, respectively.

Table V. Final Fractional Coordinates for $[(PEt_3)MCl_2]_2$ ($\times 10^5$ for M; $\times 10^4$ for Remainder) with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*
M[a]	10603 (3)	10099 (2)	9460 (2)
Cl(1)	−1849 (2)	661 (1)	−289 (1)
Cl(2)	85 (2)	2623 (1)	1545 (1)
P	3742 (2)	1340 (1)	2039 (1)
C(1)	5356 (6)	270 (4)	1967 (4)
C(2)	7189 (7)	417 (5)	2721 (4)
C(3)	3622 (7)	1469 (5)	3502 (4)
C(4)	2818 (10)	470 (5)	3994 (4)
C(5)	4691 (8)	2606 (4)	1607 (6)
C(6)	4643 (10)	2753 (6)	458 (7)

[a] M is the disordered PdPt atom.

The structure was solved by the heavy-atom method. With 2 molecules in the unit cell, space group $P2_1/n$ requires the molecules to lie on inversion centers consequently, there is equal disorder of the palladium and platinum atoms. Refinement[36] of the structure was by full-matrix least-squares calculations, initially with isotropic and finally with anisotropic thermal parameters for the non-hydrogen atoms. At an intermediate stage in the refinement, a difference map revealed all hydrogen atoms in positions close to those expected; these atoms were then positioned geometrically (C–H = 0.95 Å), and in subsequent cycles, although they were included, only an overall isotropic thermal parameter was refined for them. Refinement converged with $R = 0.030$ and $R_w = (\sum \omega \Delta^2 / \sum \omega F_0^2)^{1/2} = 0.033$. In the refinement cycles, weights were derived from the counting statistics, $w = 1/(\sigma^2 F + 0.0012 F^2)$. Scattering factors were those of Cromer and Mann[37] and Stewart, Davidson, and Simpson,[38] and allowance was made for anomalous dispersion.[39] A difference map calculated at the conclusion of the refinement was essentially featureless.

The final fractional coordinates with estimated standard deviations are given in Table V. Tables of hydrogen coordinates, anisotropic temperature factors, and a structure factors have been deposited as supplementary material.

Acknowledgment. The continued financial support of the National Sciences and Engineering Research Council of Canada (to H.C.C. and G.F.) is acknowledged with gratitude, as well as the loan of platinum compounds of Johnson Matthey Ltd. (to H.C.C.). Thanks are expressed to Drs. R. K. Boyd and G. W. Wood for obtaining the mass spectra.

Registry No. $[(PEt_3)_2PtPdCl_4]$, 95387-53-4; $[(PPr_3)_2PtPdCl_4]$, 15306-37-3; $[(PBu_3)_2PtPdCl_4]$, 15219-55-3; $[(PPh_3)_2PtPdCl_4]$, 95387-55-6; $[(PPhMe_2)_2PtPdCl_4]$, 95387-54-5; $[(PPr_3)_2PdCl_2]$, 54053-83-7; *trans*-$[(PPr_3)_2PtCl_2]$, 15977-22-7; $[(PEt_3)_2PtCl_2]$, 14177-93-6; $[(PBu_3)_2PdCl_2]$, 14977-08-3; $[(PPh_3)_2PdCl_2]$, 13965-03-2; $[(PPhMe_2)_2PdCl_2]$, 15616-85-0; $[(PBu_3)(SnCl_3)Pd(\mu\text{-}Cl)_2Pt(SnCl_3)(PBu_3)]$, 95387-56-7; $[(PBu_3)_2Pd_2(\mu\text{-}Cl)_2]$, 14882-49-6; $[(PBu_3)ClPd(\mu\text{-}Cl)_2Pt(SnCl_3)(PBu_3)]$, 95406-45-4; $[(PBu_3)(SnCl_3)Pd(\mu\text{-}Cl)_2PtCl(PBu_3)]$, 95406-46-5; Pd, 7440-05-3; Pt, 7440-06-4; Sn, 7440-31-5; CO, 630-08-0; C_5H_5N, 110-86-1; PPh_3, 603-35-0; $AsPh_3$, 603-32-7.

Supplementary Material Available: Listings of anisotropic thermal parameters, calculated hydrogen atom coordinates, and calculated and observed structure factors (13 pages). Ordering information is given on any current masthead page.

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