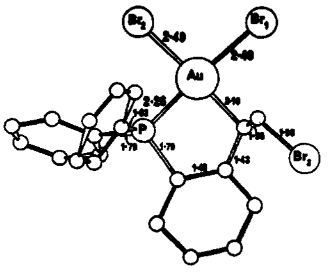


Figure 1. Stereochemistry and important bond lengths (Å) of **6**.

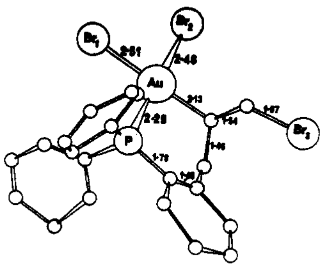


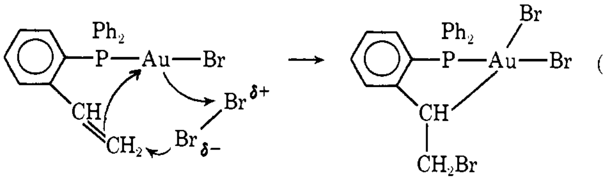
Figure 2. Stereochemistry and important bond lengths (Å) of **7**.

Crystal Data for 7. Crystals of poor quality from benzene belonged to space group *Pbca*, with $Z = 8$; $a = 15.23$, $b = 32.13$, $c = 8.87$ Å. Structure analysis was based on 1058 independent reflections (Pailred, Mo Kα) for which $F_o^2/\sigma(F_o^2) > 2.0$; least-squares refinement was carried out to a discrepancy index of 0.08; esd's average 0.006 Å (Au–Br) 0.01 Å (Au–P), 0.04 Å (Au–C), and 0.07 Å (C–C).

The molecular geometries of **6** and **7** are shown in Figures 1 and 2, together with important bond lengths. In **6**, two bromine atoms, a phosphorus atom, and the α-carbon atom of the side chain form a planar array about the metal, and the five-membered chelate ring containing the Au–C σ bond (structure I) has an envelope conformation. **7** also contains a planar-coordinated gold atom, which is attached to the β-carbon atom of the side chain to give a six-membered ring having a twist-boat conformation. The Au–C bond distances in **6** and **7** compare well with those found in $[(CH_3)_2AuOH]_4$ (2.05 Å)[5] and $(C_6F_5)_2AuCl[P(C_6H_5)_3]$ (2.12 (9), 2.18 (10) Å).[6] The Au–P distances are significantly shorter than that found in $(C_6F_5)_2AuCl[P(C_6H_5)_3]$ (2.37 (3) Å).[6] No accurately determined Au^{III}–Br distances seem to be available for comparison. The Au–Br distance trans to the σ-bonded carbon in **7** is significantly longer than that trans to phosphorus, a feature which has been observed previously in complexes containing transition metal–carbon σ bonds, and which has been ascribed to the high σ-inductive electron-donating effect of carbon as a ligand atom.[7] Complex **6** is surprisingly atypical in that its Au–Br distances are equal within experimental error.

The nmr spectrum of **6** in $CDCl_3$ shows two resonances centered at δ ~4.2 (m, 2, CH_2) and ~5.5 (m, 1, CH). Although complete analysis has not been possible, it is clear that the chemical shifts of the diastereotopic exocyclic methylene protons are very similar. The platinum complex **3** exhibits a similar nmr spectrum and therefore probably has the same five-membered chelate ring structure, though the situation is complicated in this case by the presence in solution of isomers in which the arsenic atoms are cis and trans, respectively, and also by the presence of some of the isomeric tetrabromoplatinum(IV) complex, $PtBr_4[o\text{-}(CH_3)_2AsC_6H_4CH{=}CH_2]_2$.[8]

The bromination reported here can be compared with the bromination of olefins[9] and with the oxidative addition of halogens (and other molecules) to planar metal complexes.[10] At least in nonpolar solvents, the intervention of free Br^+ or Br^- seems unlikely, and we prefer to regard the reactions as involving a concerted attack on the metal complex by a polarized bromine molecule, as shown in eq 1.



(1)

In the presence of excess methanol, bromination of AuBr(SP) yields a mixture of **6** and a methoxy complex, $AuBr_2(SP\cdot OCH_3)$, formed by substitution of the exocyclic bromine atom accompanied by ring expansion.[11] Chlorination of AuCl(SP) gives the six-membered ring compound

$$o\text{-}Ph_2\overline{PC_6H_4CHClCH_2Au}Cl_2$$

in good yield as the only isolable product. Experiments are in progress to determine the stereochemistry of the halogen additions.

Acknowledgments. We thank the Science Research Council (U. K.) for support of this work, and Dr. R. Bramley for helpful discussion.

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[11] M. A. Bennett, K. Hoskins, W. R. Kneen, R. S. Nyholm, R. Mason, P. B. Hitchcock, G. B. Robertson, and A. D. C. Towl, *J. Amer. Chem. Soc.*, 93, 4592 (1971).

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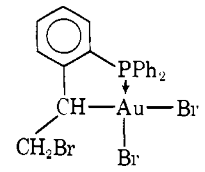
Received May 8, 1971

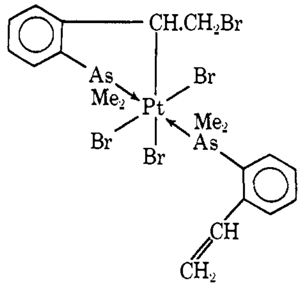
Ring Expansions in the Reactions of Transition Metal–Carbon σ-Bonded Chelate Complexes

Sir:

We wish to report an example of a molecular rearrangement in chelate rings containing a transition metal–carbon σ bond. This involves the expansion of a chelate five-membered ring to a six-membered ring accompanying solvolysis of an exocyclic bromine atom.[1]



I



II

The chelate M–C σ-bonded complexes

$\overline{\mathrm{AuBr_2[}o\text{-}\mathrm{(C_6H_5)_2PC_6H_4CH(CH_2Br)]}}$

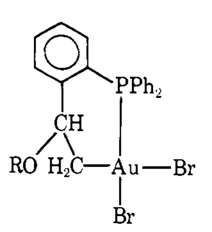
1

and

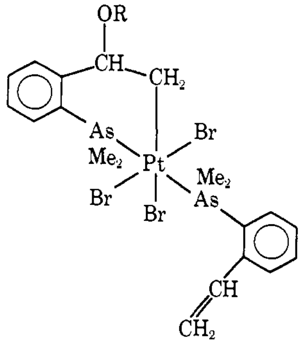
$\overline{\mathrm{PtBr_3[}o\text{-}\mathrm{(CH_3)_2AsC_6H_4CH(CH_2Br)][}o\text{-}\mathrm{(CH_3)_2AsC_6H_4CH{=}CH_2]}}$

2

are obtained by bromination of the gold(I) complex AuBr[o-$(C_6H_5)_2PC_6H_4CH{=}CH_2$] and of the platinum(II) complex $PtBr_2[o\text{-}(CH_3)_2AsC_6H_4CH{=}CH_2]_2$, respectively; their structures (I and II) are based on single-crystal X-ray and proton nmr studies.[2] The exocyclic bromine atom of **1** is replaced by OCH_3, OC_2H_5, or OH on heating with methanol, ethanol, or aqueous acetone for 8 hr. The ^{31}P decoupled 100-MHz proton nmr spectrum of the methoxy derivative **3** shows $\delta(CDCl_3)$ 2.90 (s, 3, OCH_3), 3.61 (dd, 1, J = 11 Hz, J = 2 Hz, CH of CH_2), 4.28 (dd, 1, J = 11 Hz, J = 4 Hz, CH of CH_2), 5.39 (m, 1, CHCH$_2$), 7.3–8.2 (m, 14, Ar). The main difference from the spectrum of **1**[2] is the marked inequivalence of the methylene protons, which we believe to be endocyclic in the six-membered chelate ring structure III.



III



IV

R = H, CH_3 or C_2H_5

Complex **2** is also solvolyzed on heating with methanol, ethanol,[3] or aqueous acetone for ~30 min to give the corresponding methoxy, ethoxy, and hydroxy derivatives (**4**, **5**, and **6** respectively). These reactions are considerably faster than the solvolysis of **1**, presumably owing to the higher formal positive charge of Pt(IV) compared with Au(III). The products are assigned the ring-expanded structure IV, analogous to III, on the basis of a single-crystal X-ray study of **5** described below.[4] The proton nmr spectra of **4–6** and of **3** are basically similar except that the chemical shift difference between the endocyclic methylene protons is smaller in the platinum complexes.[5] This similarity, taken with the X-ray result, provides additional support for structure III.

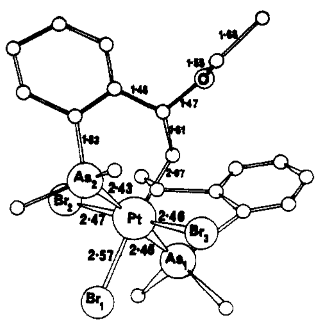


Figure 1. Stereochemistry and important bond lengths of **5**.

The crystals from ethanol belong to space group $P\bar{1}$ with $Z = 2$; $a = 10.89$, $b = 14.82$, $c = 8.92$ Å; $\alpha = 84.5$, $\beta = 107.6$; and $\gamma = 95.2°$. Structure analysis was based on 1703 independent reflections, the relative intensities of which were visually observed (Mo Kα, Weissenberg, and inclined beam oscillation methods). Least-squares refinement was carried out to $R = 0.094$; the esd's average 0.005 Å (Pt–Br and Pt–As), 0.04 Å (Pt–C and As–C), and 0.07 Å (C–C and C–O).

The molecular structure of **5** is shown in Figure 1, together with important bond lengths. The ligands are arranged in a slightly distorted octahedron about the metal atom, which is attached to the β-carbon atom of the side chain to give a six-membered chelate ring. This adopts a "twist-boat" conformation, as expected, since the metal, its attached carbon atom, and the phenylene carbon atoms have to be coplanar. The ethoxy group and one of the arsenic methyl groups occupy the bowsprit positions of the ring, which are the least hindered positions of twist-boat substituent sites. The Pt–C bond length (2.07 Å) is normal. The Pt–Br distances of the mutually trans bromine atoms are equal, their value coinciding with the covalent radius sum, but

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(1) There is one example of the expansion of a five- to a six-membered ring in a metal π complex, *i.e.*, $C_5H_5Co(C_5H_5CRR'X) - X^- \rightarrow C_5H_5\text{-}Co(C_6H_5RR')$: G. E. Herberich, G. Greiss, and H. F. Heil, *J. Organometal. Chem.*, 22, 723 (1970).

(2) M. A. Bennett, K. Hoskins, W. R. Kneen, R. S. Nyholm, P. B. Hitchcock, R. Mason, G. B. Robertson, and A. D. C. Towl, *J. Amer. Chem. Soc.*, 93, 4591 (1971).

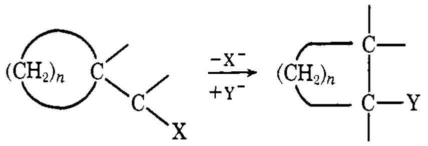
(3) M. A. Bennett, J. Chatt, G. J. Erskine, J. Lewis, R. F. Long, and R. S. Nyholm, *J. Chem. Soc. A*, 501 (1967).

(4) The structure of the ethoxy derivative obtained analogously using (o-allylphenyl)dimethylarsine, $o\text{-}CH_2{=}CHCH_2C_6H_4As(CH_3)_2$, as ligand has been reported briefly: M. A. Bennett, G. J. Erskine, J. Lewis, R. Mason, R. S. Nyholm, G. B. Robertson, and A. D. C. Towl, *Chem. Commun.*, 395 (1966). Subsequent work has shown that the complex studied by X-ray was in fact that derived from o-styryldimethylarsine, $o\text{-}CH_2{=}CHC_6H_4As(CH_3)_2$, the structure of which is reported here, and that the error arose because a sample was incorrectly labeled. Although the geometry about the metal atom, the metal–ligand distances, and the chelate geometry reported previously are correct, the assignment of the position of the ethoxy group must be disregarded. Attempts to grow single crystals of the ethoxy derivative containing (o-allylphenyl)-dimethylarsine have been unsuccessful.

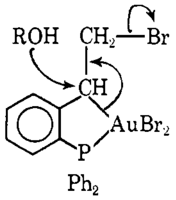
(5) The nmr of methoxy derivative **4** is as follows: δ ($CDCl_3$) 1.98–2.36 (overlapping 1:4:1 triplets, 12, As(CH_3)$_2$, J_{Pt-H} = 13 Hz), 3.14 (s, 3, OCH_3), 2.8–3.2 (complex ABX, 2, CHCH_2), 4.33 (dd, 1, CHCH$_2$, X of ABX with ^{195}Pt satellites, J_{Pt-H} = 37 Hz), 5.41 (d, 1, =CH_2, J_{cis} = 10 Hz), 5.69 (d, 1, =CH_2, J_{trans} = 17 Hz), 7.1–7.7 (m, 9, Ar and =CH).

the Pt–Br distance trans to the σ-bonded carbon atom is significantly ($\Delta/\sigma = 13.2$) greater than this. This is ascribed to the well-documented trans bond weakening, σ-inductive effect of carbon as a ligand atom which operates in planar and octahedral complexes.[6,7]

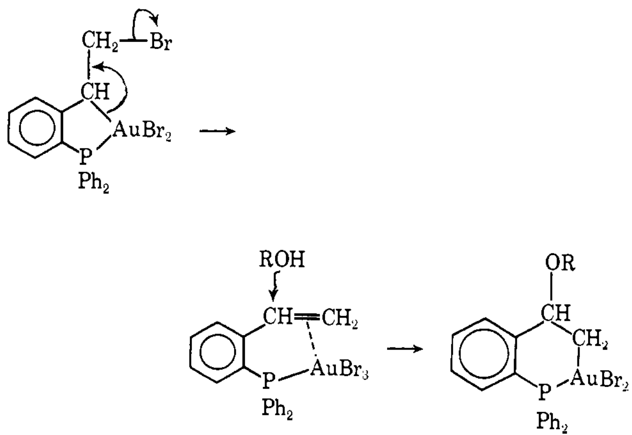
The ring expansion accompanying nucleophilic substitution of Br by OCH_3, OC_2H_5, or OH (**1** → **3**; **2** → **4**, **5**, or **6**) bears an obvious resemblance to the Wagner–Meerwein rearrangements occurring in ring expansions of cycloalkanecarbinyl systems,[8] *i.e.*



A similar mechanism involving a Wagner–Meerwein shift of the metal atom could be operative in the present case, *e.g.*



An alternative possibility[9] involves initial cis elimination of $AuBr_3$, followed by nucleophilic attack on the resulting coordinated double bond, *e.g.*



V

Experiments are in progress in an effort to distinguish between these possibilities.

Acknowledgments. We thank the Science Research Council (U. K.) for support of this work, Dr. R. Bramley for helpful discussion, and Johnson Matthey Co. (U. K.) for a generous loan of platinum.

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(6) R. Mason and A. D. C. Towl, *J. Chem. Soc. A*, 1601 (1970), and references cited therein; J. J. Daly and R. P. A. Sneeden, *ibid.*, 736 (1967).

(7) R. McWeeney, R. Mason, and A. D. C. Towl, *Discuss. Faraday Soc.*, No. 47, 20 (1969).

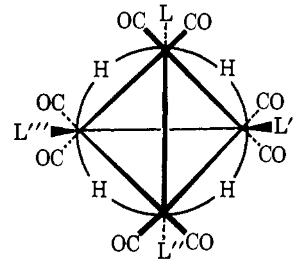
(8) C. D. Gutsche and D. Redmore, "Carbocyclic Ring Expansion Reactions," Academic Press, New York, N. Y., 1968, Chapter 2.

(9) We are indebted to a referee for calling our attention to this mechanism, which nevertheless seems to us unlikely. There is no precedent for five-coordinate gold(III)–olefin complexes such as V. If the double bond were not coordinated so that gold(III) retained its normal planar coordination, there seems to be no reason why the olefin should be susceptible to nucleophilic attack by an alcohol.

Intramolecular Tautomerism of Hydrogen in Hydrido Carbonylmetal Clusters[1]

Sir:

The spin coupling of magnetically active nuclei with hydrogen atoms is potentially useful in determining their relative position in hydrido carbonylmetal clusters. A face-bridging position for hydrogen has been postulated[2] for $H_4Re_4(CO)_{12}$ (I) on the basis of the high symmetry (T_d) required by the two observed carbonyl stretching modes. A structure of lower symmetry is indicated from the infrared spectrum for $H_4Ru_4(CO)_{12}$ (II), and several possible isomers have been discussed.[3] More recently, the report[4] of a simplified spectrum containing five carbonyl stretching bands for a sample of II of improved purity favors the D_{2d} structure shown,



II, (D_{2d}), $L = L' = L'' = L''' = CO$
III, $L = P(OCH_3)_3$; $L' = L'' = L''' = CO$
IV, $L = L' = P(OCH_3)_3$; $L'' = L''' = CO$
V, $L = L' = L'' = P(OCH_3)_3$; $L''' = CO$
VI, $L = L' = L'' = L''' = P(OCH_3)_3$

for which this number of bands is predicted. Hydrogen modes have been observed in the laser-Raman spectrum of II (at 1585 and 1290 cm^{-1}, and for the tetradeuterated derivative at 1153 and 909 cm^{-1}), confirming a bridging position for the hydrogen atoms. To gain some additional information on the location of these atoms, we have prepared derivatives substituted with $P(OCH_3)_3$ (L) to follow the coupling of metal-bonded H with ^{31}P. We chose this ligand because ^{31}P–CH_3 coupling might also be used to provide information on its relative

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(1) Work supported by National Science Foundation Grant No. 2367X. Departmental instruments used in this work were supported as follows: Varian A-60 nmr spectrometer, E. I. du Pont de Nemours and Co. and National Science Foundation Grant No. G 20207; Beckman IR-4, E. I. du Pont de Nemours and Co.; AEI MS9 mass spectrometer, National Science Foundation Grant No. GP 3672.

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(3) B. F. G. Johnson, R. D. Johnston, J. Lewis, B. H. Robinson, and G. Wilkinson, *J. Chem. Soc. A*, 2856 (1968).

(4) H. D. Kaesz, S. A. R. Knox, J. W. Koepke, and R. B. Saillant, *Chem. Commun.*, 477 (1971).