kcal/mol more stable than the plane with T replaced by BU. Using the methods above we find the best

$$\begin{pmatrix} A & T \\ BU & A \end{pmatrix}$$

plane to have a stabilization energy of −17.3 kcal/mol compared with the best

$$\begin{pmatrix} AT \\ TA \end{pmatrix}$$

energy of −18.2 kcal/mol. The difference gives $N_{BU}/N_T = \exp[-0.9 \times 10^3/1.987 \times 310] = 0.2$, in excellent agreement with experiment.

Finally, two related calculations should be mentioned. Although no details are given, Rein, McMullen, and Pollak[28] have calculated the energy of normal replication planes. In both cases they find considerable stabilization energy. Replication planes incorporating rare tautomeric forms were not considered. MacIntyre and Löwdin[29] have studied replication planes containing pairs of rare forms A*–T* and C*–G*. These might arise in the normal DNA strand by simultaneous proton tunneling in the base pair,[30] as well as by incorporation of two rare bases from the environment. Such replication planes were found to be less stable than the normal forms.

Acknowledgment. The authors are grateful to the du Pont and Monsanto Companies for Fellowships to G. E. B. and to Vanderbilt University for computing support.

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(28) R. Rein, A. I. McMullen, and M. Pollack, Abstract No. 138, Second International Biophysics Congress, Vienna, 1966.

(29) W. M. MacIntyre and P.-O. Löwdin, *Int. J. Quantum Chem.*, **2S**, 207 (1968).

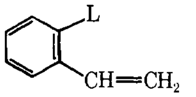
(30) P.-O. Löwdin, *Advan. Quantum Chem.*, **2**, 286 (1965).

Communications to the Editor

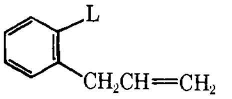
Formation of Gold(III)–Carbon σ Bonds in the Bromination of Linear Gold(I) Complexes of Olefinic Tertiary Phosphines

Sir:

The ligands *o*-styryldimethylarsine, *o*-$CH_2{=}CHC_6H_4As(CH_3)_2$ (SA; **1a**), and (*o*-allylphenyl)dimethylarsine, *o*-$CH_2{=}CHCH_2C_6H_4As(CH_3)_2$ (AA; **2a**) form both olefin-coordinated chelate complexes such as $PtBr_2$ligand and monodentate As-coordinated complexes of formula $PtBr_2(ligand)_2$.[1,2] These molecules have two potential sites for reaction with an electrophile such as bromine, the metal[3] and the double bonds.

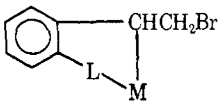


1a, L = $As(CH_3)_2$ (SA)
b, L = $P(C_6H_5)_2$ (SP)

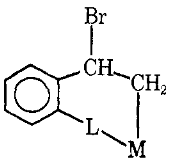


2a, L = $As(CH_3)_2$ (AA)
b, L = $P(C_6H_5)_2$ (AP)

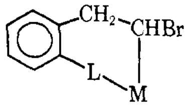
Addition of 1 equiv of bromine to $PtBr_2(SA)_2$ and $PtBr_2(AA)_2$, respectively, gives complexes of general formula $PtBr_4(ligand)_2$ which have been formulated on the basis of chemical and spectroscopic evidence[1] as octahedral tribromoplatinum(IV) complexes containing a Pt–C σ bond to one of the ortho substituents, *i.e.*, one bromine atom has added to the metal and the other has added to one of the double bonds. The precise structure of these complexes is unknown; *e.g.*, for $PtBr_4(SA)_2$ (**3**), there are three structural possibilities (I–III) for the chelate ring containing the Pt–C σ bond.



I



II



III

Prompted by the similarity between the chemistries of gold and platinum (especially the stability of their alkyls), we have studied the halogenation of the linear gold(I) complexes of *o*-styryldiphenylphosphine, *o*-$CH_2{=}CHC_6H_4P(C_6H_5)_2$ (SP; **1b**) and (*o*-allylphenyl)-diphenylphosphine, *o*-$CH_2{=}CHCH_2C_6H_4P(C_6H_5)_2$ (AP; **2b**).

The linear P-coordinated complexes AuBr(SP) (**4**) and AuBr(AP) (**5**) react with bromine in benzene at room temperature to give yellow crystals of empirical formula $AuBr_3(SP)$ (**6**) and $AuBr_3(AP)$ (**7**), respectively, which are monomeric in $CHCl_3$. The characteristic signals due to the uncoordinated olefinic protons of **4** and **5** are absent from the proton nmr spectra of **6** and **7**, and the characteristic olefinic deformation frequencies which appear in the ir spectra of **4** and **5** are absent from the spectra of **6** and **7**. Thus, **6** and **7** cannot be formulated as planar tribromogold(III) complexes[4] containing monodentate P-bonded SP or AP. The only reasonable alternative is that they are planar dibromogold(III) complexes with an Au–C σ bond to the ortho substituent, and this is confirmed by a single-crystal X-ray study of both compounds.

Crystal Data for 6. Crystals from CH_2Cl_2 belonged to space group $P2_1n$, with $Z = 4$; $a = 8.59$, $b = 13.70$, $c = 17.91$ Å; $\beta = 97.3°$. Structure analysis was based on 1705 independent reflections (Pailred diffractometer, Mo Kα) for which $F_o^2/\sigma(F_o^2) \geq 3.0$; least-squares refinement was carried out to a discrepancy index of 0.06; esd's average 0.004 Å (Au–Br), 0.008 Å (Au–P), 0.03 Å (Au–C), and 0.04 Å (C–C).

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

(2) M. A. Bennett, G. J. Erskine, and R. S. Nyholm, *ibid.*, 1260 (1967).

(3) The metal atom in planar platinum(II) complexes such as $PtCl_2[P(C_2H_5)_3]_2$ and $PtBr_2[AsCH_3(C_6H_5)_2]_2$ is halogenated to give octahedral tetrahalo complexes of the type $PtX_4(ligand)_2$ (X = Cl or Br): R. S. Nyholm, *ibid.*, 843 (1950); J. Chatt, *ibid.*, 2301 (1950).

(4) F. G. Mann and D. Purdie, *ibid.*, 1235 (1940).

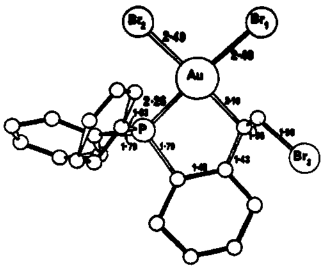


Figure 1. Stereochemistry and important bond lengths (Å) of **6**.

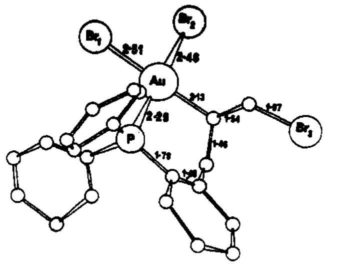


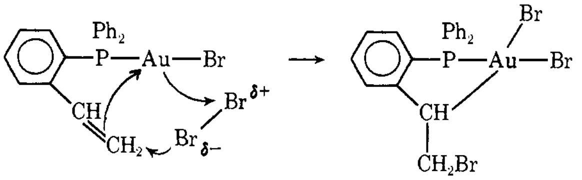
Figure 2. Stereochemistry and important bond lengths (Å) of **7**.

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 $\delta \sim 4.2$ (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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(5) G. E. Glass, J. H. Konnert, M. G. Miles, D. Britton, and R. S. Tobias, *J. Amer. Chem. Soc.*, 90, 1131 (1968).

(6) R. W. Baker and P. Pauling, *Chem. Commun.*, 745 (1969).

(7) R. McWeeny, R. Mason, and A. D. C. Towl, *Discuss. Faraday Soc.*, No. 47, 20 (1969); R. Mason and A. D. C. Towl, *J. Chem. Soc. A*, 1601 (1970).

(8) M. A. Bennett and K. Hoskins, unpublished work.

(9) P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," Elsevier, New York, N. Y., 1966, Chapter 7; R. C. Fahey, *Top. Stereochem.*, 3, 237 (1968).

(10) J. P. Collman and W. R. Roper, *Advan. Organometal. Chem.*, 7, 53 (1968); J. Halpern, *Accounts Chem. Res.*, 3, 386 (1970).

(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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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