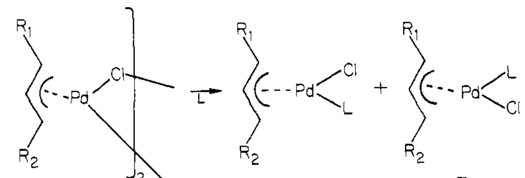
Table I. Effect of Added Ligands on Regioselectivity (4:6)[a]

ligand	equiv added[b]	4:6 ratio in coupled product
none		0.67
PPh_3	4.1	1.0
	13.2	1.0
PPh_2(*o*-anisyl)	4.6	1.0
tri-*o*-tolylphosphine	2.7	0.9
	14.2	0.3
$PMePh_2$	4.0	1.0
$P(OMe)_3$	4.6	1.0
pyridine	4.0	0.7
maleic anhydride	2.1	1.5
	4.1	1.5
	2.9	1.8[c]
	2.8	6.0[d]
	3.0	>7.0[e]

[a] All reactions performed at room temperature unless otherwise noted. [b] Per Pd. [c] 0 °C. [d] –40 °C. [e] –78 °C.

Scheme I



2 **A** **B**

added ligand prior to addition of **3**.[10,11] Initially, the effects of phosphine ligands on the reaction in THF were examined (Table I). It is notable that the addition of phosphines did *not* result in control of the regiochemistry of coupling in a pattern which could be correlated with the steric bulk of the phosphine.[11] Variation in solvent (CH_3CN, CH_2Cl_2, toluene, or hexane) also had little effect on this regiochemistry. However, as shown in Table I, equilibrating **2** with maleic anhydride prior to addition of **3** gave mixtures of coupled products in which **4** predominated. For example, equilibration of **2** (1.0555 g, 2.175 mmol) with maleic anhydride (0.5345 g, 5.454 mmol)[12] in 250 mL of dry, air-free THF under N_2 at -78 °C, followed by slow addition of a cooled solution of **3** (1.0 g, 2.9 mmol in 50 mL THF, also at -78 °C), blocked formation of **1** and gave **4** and **6** in a ratio of at least 7:1 as determined by ^1H NMR. Purification via liquid chromatography on silica gel, eluting with ethyl acetate/hexane, gave a 96% combined yield of coupling product as a viscous oil from which **4** was isolated (78%) by crystallization followed by high-performance LC separation of the mother liquors (recrystallization from EtOAc/EtOH, mp 92-93 °C).[13]

Diene **4** was hydrogenated using PtO_2/EtOAc at 3 atm of H_2 for 40 h. The saturated ketal was recovered in quantitative yield[14] and hydrolyzed by refluxing in aqueous 1,2-dimethoxyethane, acidified with sulfuric acid. The product was purified by liquid chromatography (silica gel, ethyl acetate/hexane) and recrystallized from ethanol (mp 128-129 °C). Its spectral properties (^1H, ^{13}C NMR) were identical with those of an authentic sample (mmp 128-129 °C), confirming that the compound formed possesses the natural steroidal configuration at C-20.[15]

The formation of **4** (with the *R* configuration at C-20) proves that alkylation at Pd precedes C-C bond formation. The origin of regiocontrol by added ligand of this coupling reaction is believed to result from a geometrical preference of the (π-allyl)(ligand)PdCl precursor, A or B (Scheme I).[16] In this scheme, transmetalation to A or B results in replacement of –Cl by the alkenyl group and is followed by rapid reductive elmination of product. We propose that steric differences between R_1 and R_2 give rise to a distortion of the π-allylic ligand in **2** by movement of Pd closer to the sterically less congested terminus. This perturbed geometry dictates the preferred ligated complex (A or B) depending on the donor/acceptor properties of that ligand,[17,18] hence establishing regiocontrol in these "syn" coupling reactions.

The scope of this reaction as a synthetic procedure is now under examination, and further investigation of the origin of regiocontrol is proceeding.[19]

Acknowledgment. We gratefully acknowledge support for this research provided by the National Science Foundation, Grant No. CHE-79-00996.

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[10] We suggest that (allyl)Pd-R can readily undergo β-hydrogen transfer from R to Pd, leading to formation of olefin. Coordination of ligands such as maleic anhydride should suppress this β-hydrogen transfer and hence olefin byproduct formation. It is significant to note that dimethylcadmium, in which the possibility for β-H transfer to Pd is obviated, can be used to couple methyl groups with π-allylic palladium species: Castanet, Y.; Petit, F. *Tetrahedron Lett.* **1979**, 3221.

[11] The regiochemistry of (anti) nucleophilic attack on (π-allyl)Pd complexes in the presence of phosphines has been related to the steric bulk of the added ligand. Trost, B. M.; Weber, L.; Strege, P. E.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3416.

[12] Numata, S.; Kurosawa, H. *J. Organomet. Chem.* **1977**, *131*, 301.

[13] ^{13}C NMR shows **4** to be a single compound: ^1H NMR ($CDCl_3$) δ 5.22–5.42 (m, 3), 3.91 (s, 4), 2.78 (br m, 1), 1.0–2.0 (m, 23), 1.07 (d, 3, J = 8 Hz), 0.88 (s, 3), 0.81 (s, 6), 0.75 (s, 3). Diene **6** was obtained by preparative high-performance LC: ^1H NMR (C_6D_6) δ 5.41 (br m, 3), 3.58 (s, 4), 3.13 (br m, 1), 1.70 (d, 3, J = 7.0 Hz, of finely split d), 1.2–2.3 (br m, 23), 0.94 (s, 3), 0.88 (2s, 6), 0.71 (s, 3).

[14] The Δ^{16} monoolefin was recovered if hydrogenation was stopped after 2 h. ^1H NMR ($CDCl_3$) shows vinylic resonance as a multiplet at δ 5.18–5.26.

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[16] Numata and Kurosawa[11] have inferred the existence (in solution) of such geometrical isomers (L = tertiary phosphine) from ^1H NMR data.

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[18] Yamamoto, T.; Yamamoto, A.; Ikeda, S. *J. Am. Chem. Soc.* **1971**, *93*, 3350.

[19] Preliminary investigations reveal that a variety of Pd(II) or Pd(0) complexes can serve as precursors of catalysts for coupling allylic halides or acetates and alkenylzirconium species: Hayasi, Y.; Temple, J. S.; Schwartz, J., unpublished results.

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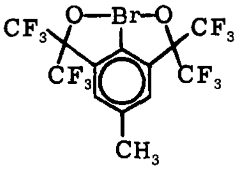
Received April 7, 1980

A Dialkoxyarylbrominane. The First Example of an Organic 10-Br-3 Species[1]

Sir:

We report the isolation and characterization of the first organobrominane, dialkoxyarylbrominane **1**, a 10-Br-3 species of



1

surprising stability. Although analogous iodine species have long been known, with a variety of substituent types,[2] all reported 10-Br-3 species, such as BrF_3, $Br(NO_3)_3$,[3] $Br(OSO_2F)_3$,[4] and $Br(OSeF_5)_3$,[5] contain fluorine or other very electronegative inorganic ligands.

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[1] Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Algria, A.; Kochi, J. K. *J. Am. Chem. Soc.*, in press. They describe the classification scheme applied here to a 10-electron bromine species with three ligands to bromine (10-Br-3).

[2] (a) Agosta, W. C. *Tetrahedron Lett.*, **1965**, *31*, 2681. (b) Baker, G. P.; Mann, F. G.; Sheppard, N.; Tetlow, A. J. *J. Chem. Soc.* **1965**, 3721. (c) Koser, G. F.; Wettach, R. H. *J. Org. Chem.* **1980**, *45*, 1542. Koser, G. F.; Wettach, R. H.; Smith, C. S. *Ibid.* **1980**, *45*, 1544.

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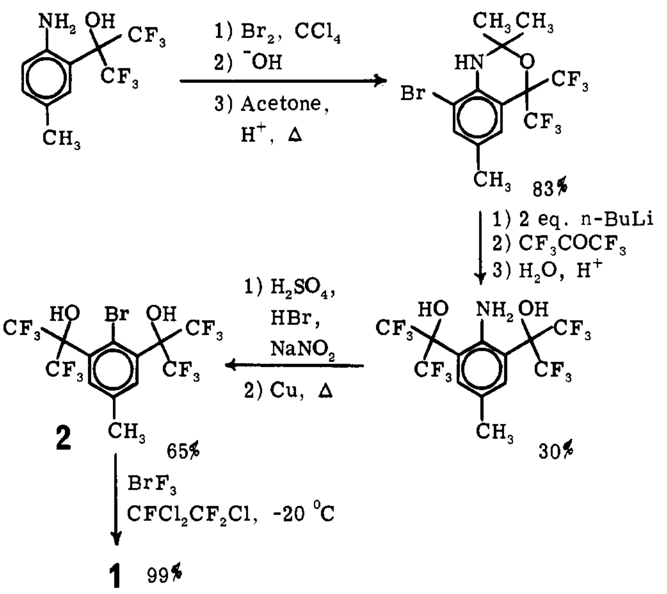
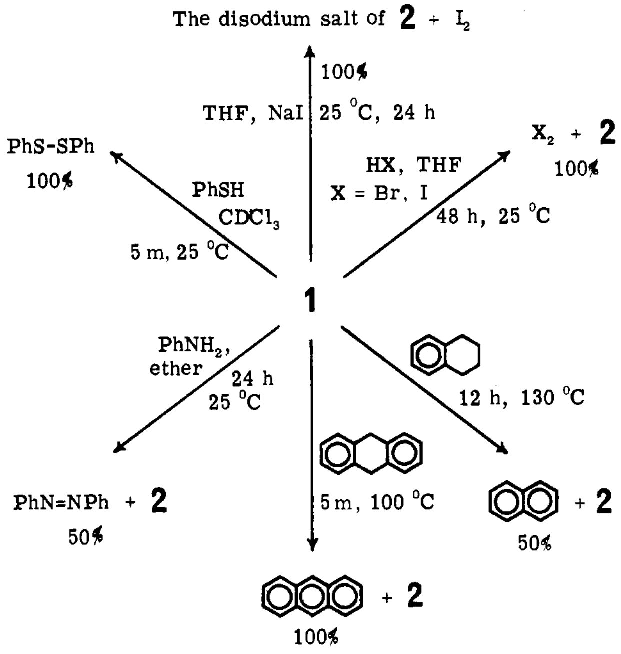
Scheme I



Scheme II



The synthesis of **1** was effected by the route of Scheme I.[6,7] Crystalline **1**, mp 153–154 °C, is stable indefinitely at room temperature and may be sublimed at 60 °C (3 torr). The ^{19}F NMR singlet at −75.8 ppm[8] assigned to the equivalent CF_3 is upfield from that of the bromo diol **2** (−73.0 ppm). The infrared spectrum shows no hydroxy absorption. The mass spectrum shows a sizable molecular ion, *m/e* 502, and 500, and a prominent fragmentation peak at *m/e* 433, and 431 corresponding to the loss of one CF_3 group. The solid brominane **1** is unreactive toward atmospheric moisture. A sample of **1** in tetrahydrofuran did not show any change in the ^{19}F NMR spectra in the presence of water, dilute HCl, or dilute aqueous NaOH at room temperature for 1 day. The brominane **1** is a mild oxidizing reagent. Some of its reactions are shown in Scheme II.[9]

The spectroscopic and chemical evidence presented here provides a compelling case for the proposed structure for brominane **1**. Further studies on the structure and reactivity of brominanes are currently under way in this laboratory.

Acknowledgment. This research was supported in part by a grant from the National Science Foundation, CHE-7905692. We acknowledge the contributions of Dr. Ronald L. Amey in working out the earlier steps in the synthesis of the tridentate ligand used here.

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Received August 25, 1980

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(6) The details of the synthesis of this generally useful tridentate ligand, used here for brominane **1**, will be published elsewhere: Nguyen, T. T.; Amey, R. L.; Martin, J. C. *J. Org. Chem.*, manuscript in preparation.

(7) Anal. ($C_{13}H_5O_2BrF_{12}$) C, H, Br, F; IR ($CHCl_3$) 1239 (m), 1084 (s), 1049 (m), 855 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.65 (s, 3, CH_3), 7.7 (s, 2, Ar H); ^{19}F NMR ($CDCl_3$) Φ −75.8 (s); mass spectrum (10 eV) *m/e* (relative intensity) 502, 500 (1.7, $M^{+\cdot}$), 431, 435 (100, $M^{+\cdot} - CF_3$), 295, 293 (7.0, $M^{+\cdot} - 3CF_3$).

(8) Chemical shifts are reported in ppm downfield of $CFCl_3$. Negative values are therefore upfield of $CFCl_3$ in accord with IUPAC recommendations: *Org. Magn. Reson.* **1978**, *11*, 267.

(9) The yields shown here were obtained by NMR. The products were identified by comparison with authentic samples.

Highly Luminescent Polypyridyl Complexes of Osmium(II)

Sir:

Transition-metal complexes which have low-lying metal to ligand charge-transfer (MLCT) excited states have played a pivotal role in demonstrating the use of molecular excited states in light energy conversion processes.[1,2] Experiments so far have relied primarily on $Ru(bpy)_3{}^{2+}$ (bpy is 2,2′-bipyridine), $Ru(phen)_3{}^{2+}$ (phen is 1,10-phenanthroline), and their ligand-substituted derivatives. The ruthenium complexes have many desirable features including high chemical and photochemical stability, a high light absorptivity in the visible region, the existence of relatively long-lived MLCT excited states, and chemically accessible ground- and excited-state redox properties.

One noticeable absence in this area has been the systematic development of new, stable chemical systems having exploitable excited states whose properties can be modified by simple alterations of the ligands. The development of new systems is essential in order to uncover new reaction pathways and to help define the fundamental photochemical and photophysical properties of MLCT excited states.

An obvious place to search for new MLCT excited states is in the chemistry of osmium where ground-state redox properties are similar to those of related ruthenium complexes and chemical stability is higher. However, spin–orbit coupling is considerably greater for osmium compared to ruthenium which is expected to enhance both radiative and nonradiative decay rates for triplet–singlet transitions and thus shorten excited-state lifetimes.[3] In fact, lifetimes for the MLCT excited states of $Os(bpy)_3{}^{2+}$, $Os(phen)_3{}^{2+}$, and related substituted ligand derivatives are considerably shorter than those of their ruthenium analogues.[4] We report that the lifetimes of osmium(II) MLCT excited states can be enhanced remarkably by replacing one of the polypyridyl ligands by stronger π acceptors such as acetonitrile or alkyl-

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(2) See, for example: (a) DeLaive, P. J.; Sullivan, B. P.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1979**, *101*, 4007. (b) Durham, B.; Dressick, W. J.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1979**, *8*, 381. (c) Kalyanasundaran, K.; Grätzel, M. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 701. (d) Lin, C. T.; Sutin, N. *J. Phys. Chem.* **1976**, *80*, 97.

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