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Preliminary communication

SYNTHESIS OF BIS(*ortho-C,N*)AZOARENE COMPLEXES WITH A "SPIRANE" PALLADIUM ATOM BY THE REACTION BETWEEN ORGANOMERCURIALS AND A DIBENZYLIDENEACETONE PALLADIUM(0) COMPLEX

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Summary

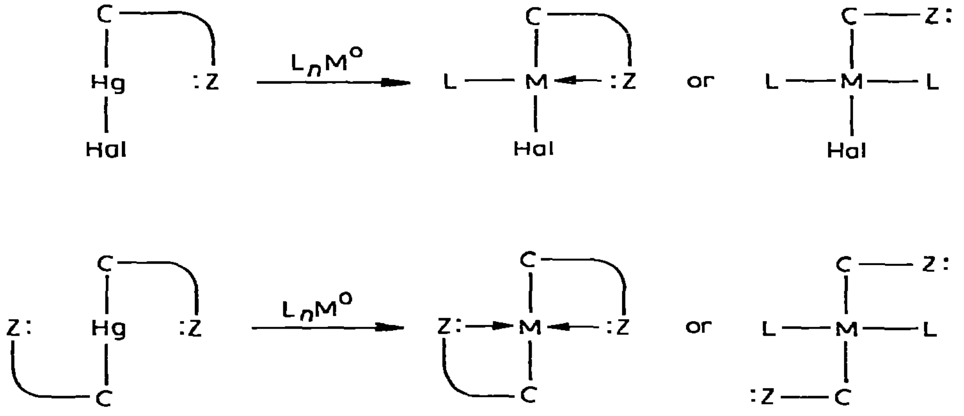
Diarylmercurials having an azo group in *ortho*-positions react readily with the dibenzylideneacetone complex of zero-valent palladium, $Pd_2(DBA)_3$, to give metallic mercury and di-σ-(2-azoaryl)palladium(II) complexes in good yields.

Recently we have shown [1] that different organomercurials react under mild conditions with zero-valent complexes of platinum or palladium to give σ derivatives of these metals as final products:

$$L_nM^0 + RHgR' \rightarrow L_2MR'R + Hg^0 + (n\text{-}2)\,L$$

The stability of σ-organo-transition metals is known to depend strongly on the nature of other ligands coordinated at the metal. When, as in most cases studied, L = Ph_3P, bis-phosphine complexes will result. Another kind of stabilization is

SCHEME 1

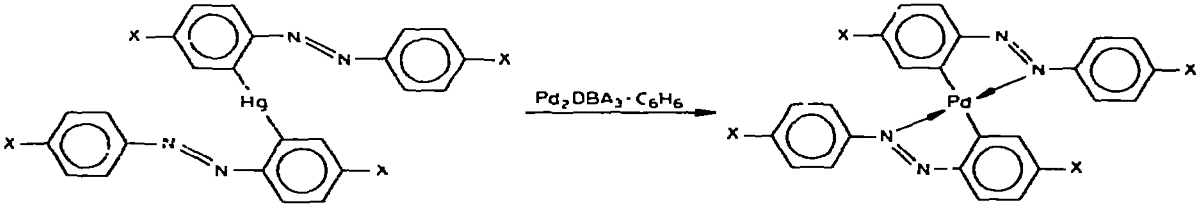


possible, however, due to intramolecular chelation through some electron-donating groups properly situated. Two reaction pathways can be depicted as shown in Scheme 1. Whether the open or chelated form will result depends on the relative ligating properties of the intramolecularly chelating group Z and free ligand L. Up until now, both types of behavior have been met.

One interesting application of this approach is the preparation of compounds with the metal atom doubly σ-bonded to carbon. Bis-chelated systems cannot be easily prepared otherwise. This one-step synthesis should start from the organomercurials R_2Hg with electron-donating atoms positioned suitably to close chelate rings. A 5-membered cycle is regarded as the optimal one but 6- and 4-membered cycles seem to be suitable, too.

Essential is the choice of the ligand L. The ligand which is loosely bound to the metal but can be readily removed from the coordination sphere will be the best. A nearly ideal ligand for this purpose seems to be dibenzylideneacetone whose Pd^0 [2-4] and Pt^0 [5, 6] complexes have been described. Like phosphine zero-valent complexes, $Pd(DBA)_n$ reacts readily with organomercurials but the stable organopalladiums can be obtained only when stabilizing ligands like phenanthroline are present.

The designed compounds with a "spirane" metal atom have been prepared in high yield by treating bis(2-arylazo)arylmercury with $Pd_2(DBA)_3 \cdot C_6H_6$ [3] in benzene at room temperature. *ortho*-Mercurated azoarenes were obtained by direct mercuration using mercuric acetate in methanol, following the observation by Rausch et al. [7]. Azoarylmercuric chlorides undergo ready symmetrization when treated with NaI in acetone, probably due to intramolecular nitrogen coordination to mercury in these salts.



Two similar palladium complexes were prepared, X being H or CH_3. Vibrational spectra are most informative for this kind of structure. In general, IR and Raman spectra of these bis-chelated compounds are very similar to the spectra of dimeric σ-azoarenepalladium chlorides, products of Cope—Siekman direct metallation [8, 9]. Of special significance is the band corresponding to the stretching of N=N double bond coordinated to the metal within the chelate ring which is observed in the region 1440-1370 nm and is the strongest absorption in the Raman spectra. The low-frequency region displays significant differences. More details of these spectra will be discussed in a forthcoming paper by Lokshin et al.

Some years ago Pauson and his coworkers [10] reported the preparation of two compounds which were assigned the bis-chelate structure, X being CH_3 or CH_3O. They obtained these products in an unexpected way in low yield, when σ-*C*,*N*-azoarenepalladium chloride dimers were treated with $Na_2Fe(CO)_4$. Our *p*-

tolyl compound from its m.p. and IR spectrum is different from Pauson's. The method of preparation here described seems to be the most direct and ambiguous one. The reason for this difference might be *cis—trans* isomerism in the planar square around the metal atom. We are inclined to believe the new complexes reported in this paper have a *trans*-configuration. One platinum analogue was prepared in the same way.

Finally, we wish to emphasize the usefulness of this reaction for the purposes of synthesizing dibenzylideneacetonepalladium(0) and -platinum(0) complexes which virtually behave as a substitute for the free active metal atom.

Experimental

2-Chloromercuri-4,4'-dimethylazobenzene (I)

2.1 g (10 mmol) of 4,4'-dimethylazobenzene and 3.2 g (10 mmol) of mercuric acetate, suspended in 30 ml CH_3OH, were refluxed for 16 h, diluted to 300 ml and heated until the precipitate dissolved. The addition of LiCl in methanol gave the chloride which was filtered off and washed with ether. 2.3 g (53%) of crude I was obtained, recrystallisation from benzene gave m.p. 228-229 °C. Found: C, 37.62; H, 3.10. $C_{14}H_{13}ClHgN_2$ calcd.: C, 37.76; H, 2.94%.

Bis(2-phenylazo)phenylmercury (II)

To 2.0 g (4.8 mmol) of 2-chloromercuriazobenzene [7] in acetone 4.0 g NaI was added. After 3 days the solution was evaporated, the residue washed with water, dried in vacuo and run through a short silica gel column using benzene as eluent. The yield of II was 1.1 g (77%), m.p. 147-149 °C, lit. 144-146° [11].

Bis(2-p-tolylazo-5-methyl)phenylmercury (III).

Similarly prepared was 0.63 g (60%) of III from 1.5 g (3.4 mmol) of I. After purification by thick-layered chromatography on silica gel (eluent light petroleum/benzene) the compound of m.p. 247 °C was obtained. Found: C, 54.16; H, 4.23; Hg, 31.82. $C_{28}H_{26}HgN_4$ calcd.: C, 54.32; H, 4.23; Hg, 32.39%.

Bis-o-C,N-(azobenzene)palladium (IV)

0.563 g (1 mmol) of II and 0.5 g (0.5 mmol) of $Pd_2(DBA)_3 \cdot C_6H_6$ suspended in benzene, were stirred under argon for 16 h. Metallic mercury (about 200 mg) separated, the filtrate was run through a short SiO_2 column and the product was eluted with benzene. 0.375 g (80%) of pure IV were obtained as bright deep-red crystals, for analysis the sample was recrystallized from light petroleum/benzene, m.p. 163-164.5° (dec.). Found: C, 60.40; H, 3.78; N, 11.58; Pd, 23.05. $C_{24}H_{18}N_4Pd$ calcd.: C, 61.46; H, 3.87; N, 11.95; Pd, 22.69%.

Bis-o-C,N-(azo-p,p'-toluene)palladium (V)

This compound was prepared in the same way as IV. From 0.230 g (0.19 mmol) of III and 0.190 g (0.19 mmol) of $Pd_2DBA_3 \cdot C_6H_6$ were obtained without chromatography, 170 mg (85%) of V as bright deep-red crystals, m.p. 172-176° (dec.). Found: C, 63.96; H, 4.97; N, 10.46; Pd, 20.66. $C_{28}H_{26}N_4Pd$ calcd.: C, 64.06; H, 4.99; N, 10.67; Pd, 20.27%.

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