Journal of Organometallic Chemistry, 61 (1973) C62–C64

Preliminary communication

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ortho-Palladated and *ortho*-platinated complexes of diaryl thioketones

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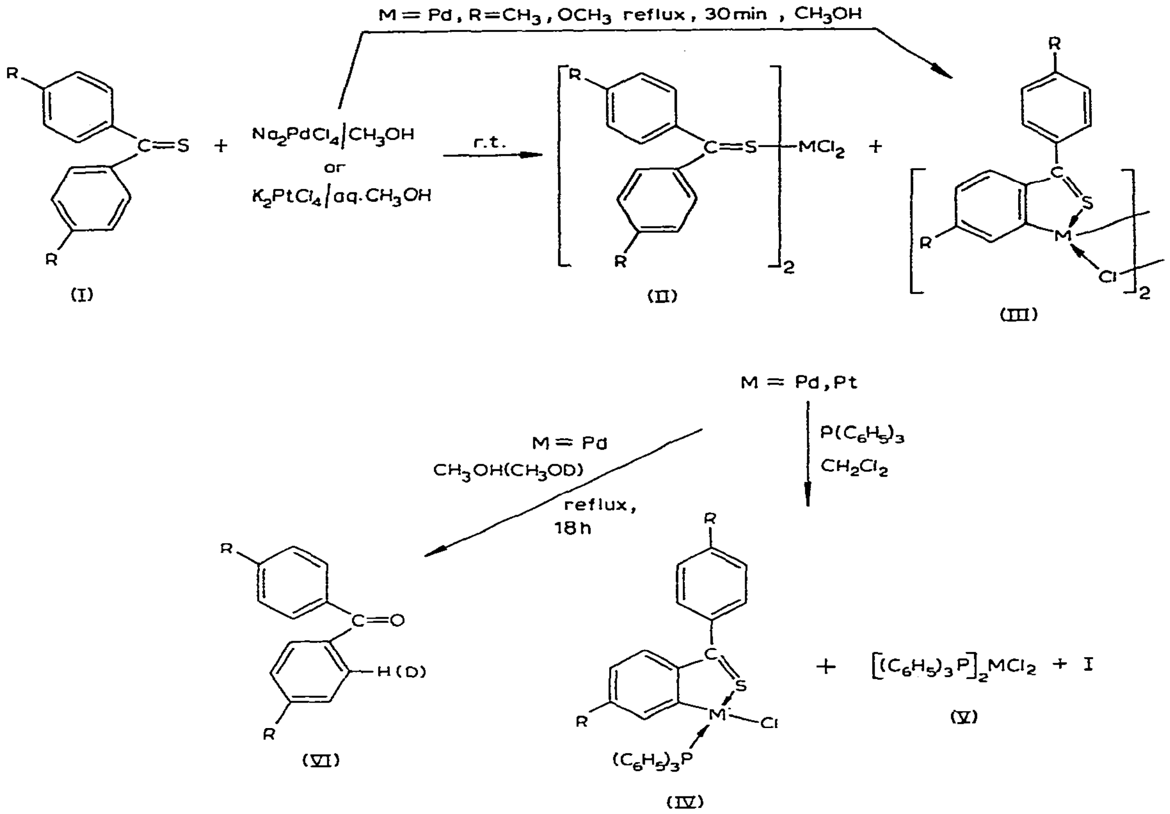
(Received August 21st, 1973)

SUMMARY

The first sulfur-donor ligand *ortho*-metalated complexes of palladium and platinum have been synthesized from thiobenzophenones. A new and convenient preparation of mono-deuterio aromatic ketones is also reported.

At least three recent unsuccessful attempts to prepare sulfur donor ligand *ortho*-metalated complexes of palladium have been reported in the literature. Benzyl thioethers were used as the reactant ligands in all cases[1–3]. This communication describes the first examples of sulfur donor ligand *ortho*-palladated and *ortho*-platinated complexes, obtained by treatment of diaryl thioketones with the appropriate metal halide.

Addition of a thiobenzophenone (I, R = H, CH_3, OCH_3, $N(CH_3)_2$, Scheme 1) to an equimolar amount of sodium tetrachloropalladate in methanol at room temperature gave a mixture of bis(thiobenzophenone)palladium chloride [II, M = Pd] and the *ortho*-metalated complex III [M = Pd]. These reactions were complete within 10 minutes. Isolation of III [M = Pd], free from traces of II, proved difficult upon work-up of the product mixture. However, pure III [M = Pd, R = CH_3 (m.p. 237–239°, 61% yield), OCH_3 (m.p. 261–263°, 54% yield)] was readily obtained by simply heating the reactants in methanol for 30 min. [III, M = Pd, R = CH_3. Found: C, 49.10; H, 3.79; Cl, 10.01; S, 8.73. $C_{30}H_{26}Cl_2Pd_2S_2$ calcd.: C, 49.06; H, 3.57; Cl, 9.66; S, 8.73%; III, M = Pd, R = OCH_3, Found: C, 45.60; H, 3.18; Cl, 8.72; S, 7,90. $C_{30}H_{26}Cl_2O_4Pd_2S_2$ calcd.: C, 45.14; H, 3.28; Cl, 8.88; S, 8.03%.] The IR thiocarbonyl stretching absorption of I experienced the expected shift to lower frequency upon complexation [*e.g.* I, R = OCH_3, ν(CS) 1217 cm^{-1}; III, M = Pd, R = OCH_3, ν(CS) 1184 cm^{-1} (KBr)]. These *ortho*-metalated complexes were insufficiently soluble for proton NMR purposes. However, treatment of a mixture of II and III with triphenylphosphine in methylene chloride at room temperature for 30 min resulted in cleavage of the bridge of III [M = Pd] to afford the more soluble *ortho*-metalated



complexes IV [M = Pd, R = CH_3 (40%), OCH_3 (43%)] By-products of these reactions were the regenerated thiobenzophenone and the known[4] *trans*-bis(triphenylphosphine)palladium chloride [V, M = Pd; note that complexes of type IV could also be obtained directly from III, without requiring the separation of IV from V and I, but such separations were exceedingly simple to effect]. The cyclopalladated complexes IV [M = Pd, R = OCH_3, m.p. 194–197°. Found: C, 59.99; H, 4.27; Cl, 5.44; P, 4.27; S, 4.27; mol. wt. 691. $C_{33}H_{28}ClO_2$-PPdS calcd.: C, 59.92; H, 4.26; Cl, 5.36; P, 4.68; S, 4.84; mol. wt. 661.5; IV, M = Pd, R = CH_3, m.p. 177–179°. Found: C, 63.40; H, 4.46; Cl, 5.48; S, 5.18. $C_{33}H_{28}ClPPdS$ calcd.: C, 62.98; H, 4.48; Cl, 5.63; S, 5.09%] were orange-red to red in color and air-stable. The proton NMR($CDCl_3$) of IV, M = Pd, R = OCH_3, displayed two singlets at δ 3.85 and 4.00 which are assigned to the methoxy groups of the palladium-substituted and unsubstituted benzene rings, respectively. Integration of the spectrum gave a ratio of 6/22 for the methoxy to aromatic protons. The signals for the two methyl groups of IV, M = Pd, R = CH_3, appeared at δ 2.38 and 2.46 [$CDCl_3$, δ 2.37 for the methyl groups of I, R = CH_3].

When a mixture of II and III [M = Pd, R = H, CH_3, OCH_3] was refluxed in methanol for 18 h, the ketone VI was formed in 80–97% yield. The benzophenone could also be obtained by refluxing a mixture of I and $PdCl_4^{2-}$ in methanol for the same length of time, *i.e.* without isolating II or III. In fact, thioacetophenone and *p*-methoxythioacetophenone react at room temperature in methanol to afford the corresponding carbonyl compounds, but not II or III. 4,4'-Dimethoxybenzophenone [VI, R = OCH_3] was also obtained when I was treated with $PdCl_4^{2-}$ in dry methanol ["absolute" methanol used in reactions described above was refluxed over magnesium methoxide and then distilled under nitrogen]. In addition, 2-deuterio-4,4'-dimethoxybenzophenone was isolated in 82% yield from treatment of II and III (or I, R = OCH_3, and $PdCl_4^{2-}$) in refluxing CH_3OD. Similarly, I, R = CH_3, gave 2-deuterio-4,4'-dimethyl benzophenone [VI, R = CH_3] in 84% yield. Thus, this method represents a convenient, new approach to *ortho*-deuterio aromatic ketones.

Treatment of I, R = CH_3, OCH_3, with potassium tetrachloroplatinate in aqueous methanol at room temperature gave II and III [M = Pt, R = CH_3, OCH_3], and subsequent reaction of the latter mixture with triphenylphosphine afforded IV [M = Pt, R = CH_3 (31%), OCH_3 (59%)], I, and the known bis(triphenylphosphine)platinum chloride. The pertinent data for the *ortho*-platinated complexes IV include: R = OCH_3, m.p. 205–207°. Found: C, 52.44; H, 3.65; Cl, 4.87; S, 4.66. $C_{33}H_{28}ClO_2PPtS$ calcd.: C, 52.84; H, 3.76; Cl, 4.73; S, 4.27%. NMR($CDCl_3$) δ 3.72, 3.85 (singlets, methoxy groups); R = CH_3. m.p. 183–185°. Found: C, 54.93; H, 4.00; Cl, 4.88; S, 3.98. $C_{33}H_{28}ClPPtS$ calcd.: C, 55.18; H, 3.93; Cl, 4.93; S, 4.46%; NMR($CDCl_3$) δ 2.25, and 2.38 (singlets, methyl groups).

ACKNOWLEDGMENT

The author is grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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