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Preliminary communication

PHOSPHITE ADDITION TO ORGANOMETALLIC CATIONS TO GIVE PHOSPHONIUM ADDUCTS

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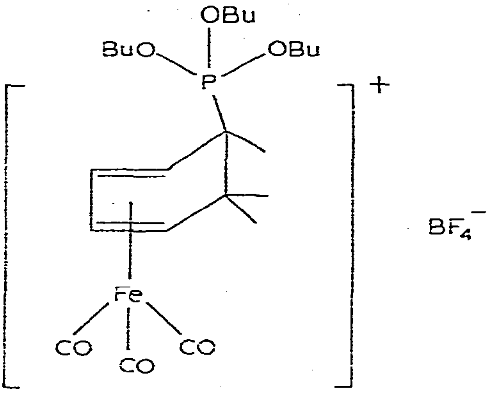
Summary

Addition of tri-n-butylphosphite to $[(C_6H_7)Fe(CO)_3]BF_4$, $[(C_6H_6OMe)Fe(CO)_3]BF_4$, and $[(C_7H_7)Cr(CO)_3]BF_4$ has yielded novel phosphonium salts; which are remarkably stable.

Nucleophilic addition of tertiary phosphines to coordinated π-hydrocarbon molecules has recently led to a variety of novel phosphonium adducts [1—7]. The first example of addition of an arsine to a π-ligand has also been reported using the dicarbonylnitrosyl(benzocyclobutadiene)iron cation as substrate [3]. Since the analogous addition of phosphites is currently unknown, we report here the reaction of tri-n-butylphosphite with $[(C_6H_7)Fe(CO)_3]BF_4$ (Ia), $[(C_6H_6OMe)Fe(CO)_3]BF_4$ (Ib), and $[(C_7H_7)Cr(CO)_3]BF_4$ (II).

Dropwise addition of an equimolar amount of tri-n-butylphosphite to a solution of $[(C_6H_7)Fe(CO)_3]BF_4$ (Ia, 100 mg) in acetone led to a pale yellow solution. Chromatography on an alumina H column followed by evaporation gave a pale yellow oil (124 mg) which analysed for the adduct $[\{(C_6H_7 \cdot P(OBu)_3\}Fe(CO)_3]BF_4$ (III). (Found: C, 45.3; H, 6.3. $C_{21}H_{34}FeO_6PBF_4$ calcd.: C, 45.3; H, 6.1%.) Its IR spectrum in acetone showed two strong bands at 2055 and 1980 cm^{-1} which are very close to those known for the analogous tri-n-butylphosphine adduct. Formulation as a BF_4^- salt was confirmed by the presence of a strong band at 1060 cm^{-1} in a nujol mull. The ^1H NMR spectrum in acetone-d_6 (multiplets centred at τ ca. 4.21, 5.30, and 6.17 ppm) is also consistent with the adduct structure.

Isolation of adduct III is remarkable since it is a characterised phosphonium adduct containing an aliphatic phosphite. Such phosphonium adducts generally undergo a spontaneous Arbusov reaction to give phosphonates. The present observation may therefore provide a further example of stabilization of an organic species via coordination to the $Fe(CO)_3$ group. Another favourable feature is that the BF_4^- ion is not expected to provide nucleophilic assistance for



(III)

the elimination. Interestingly the field-desorption (FD) mass spectrum of III shows only one significant peak at *m/e* 412, which corresponds to the molecular ion expected for the phosphonate $[\{C_6H_7 \cdot P(=O)(OC_4H_9)_2\}Fe(CO)_3]$. Arbusov elimination has apparently occurred within the mass spectrometer.

Reaction of tri-n-butylphosphite with $[(C_6H_6OMe)Fe(CO)_3]BF_4$ (Ib) yields an adduct analogous to III (ν(CO) in acetone: 2055 and 1980 cm^{-1}; *m/e* 442 in the FD mass spectrum again indicates subsequent Arbusov elimination).

Formation of stable phosphonium adducts with tri-n-butylphosphite is not limited to the iron triad, but also occurs with $[(C_7H_7)Cr(CO)_3]BF_4$ (II). Reaction in dichloromethane followed by addition of ether gave red crystalline plates (m.p. 68–69°C) of $[\{C_7H_7 \cdot P(OBu)_3\}Cr(CO)_3]BF_4$ (IV) in good yield. (Found: C, 47.1; H, 5.9. $C_{22}H_{34}CrO_6PBF_4$ calcd.: C, 46.8; H, 6.0%.) Its IR spectrum showed the presence of the BF_4^- anion, while the ν(CO) bands at 1990, 1935 and 1905 cm^{-1} are very similar to those reported for the related tri-n-butylphosphine adduct. Preliminary kinetic measurements indicate that $P(OBu)_3$ adds to II approximately 8000 times more slowly than does PBu_3, in keeping with their usual nucleophilic order.

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