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Preliminary communication

PHOSPHONIUM ADDUCT FORMATION WITH TRICARBONYL-(TROPYLIUM) CATIONS OF METALS IN GROUP VI

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Summary

Contrary to previous reports, formation of the phosphonium adducts $[(C_7H_7PBu_3)M(CO)_3]^+$ is shown to be the first detectable reaction on treating each of the $[(C_7H_7)M(CO)_3]^+$ (M = Cr, Mo and W) cations with tri-n-butylphosphine.

Recent studies [1-3] report the contrasting reaction behaviour of the cations $[(C_7H_7)M(CO)_3]^+$ (M = Cr, Mo) towards tertiary phosphine nucleophiles. Ring-addition occurs on $[(C_7H_7)Cr(CO)_3]BF_4$ yielding red phosphonium adducts of the type $[(C_7H_7PR_3)Cr(CO)_3]BF_4$ (Ia: IR bands at ca. 1990, 1930 and 1900 cm^{-1}) [1]. On the other hand, with the analogous molybdenum cation only carbonyl- or ring-displacement processes have been observed [2,3], producing the species $[(C_7H_7)Mo(CO)_2(PR_3)]BF_4$ (IIb: IR bands at ca. 2023 and 1984 cm^{-1}) and $[(PR_3)_3Mo(CO)_3]$ (IIIb: IR bands at ca. 1930 and 1835 cm^{-1}), respectively. Contrary to these previous reports, we now wish to demonstrate that phosphonium adduct formation (eq. 1) is the first detectable reaction when each of the cations $[(C_7H_7)M(CO)_3]^+$ (M = Cr, Mo and W) is treated with tri-n-butylphosphine.

$$[(C_7H_7)M(CO)_3]BF_4 + PBu_3 \rightarrow [(C_7H_7PBu_3)M(CO)_3]BF_4 \qquad (1)$$

On mixing equimolar acetone solutions (ca. 10^{-2} *M*) of $[(C_7H_7)M(CO)_3]BF_4$ (M = Cr, Mo and W) and tri-n-butylphosphine at room temperature under nitrogen, an immediate colour change from yellow to red was observed in all cases. The similarity of the IR spectra of these reaction solutions (Table 1) indicated uniform and quantitative conversion to the phosphonium adducts Ia, Ib and Ic. The chromium adduct Ia could be readily isolated and characterised using the procedure described by Hackett et al. [1].

Isolation of a pure sample of the molybdenum adduct Ib was complicated

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TABLE 1

IR CARBONYL BANDS OBSERVED ON MIXING EQUIMOLAR SOLUTIONS (10^{-2} *M*) OF $[(C_7H_7)M(CO)_3]BF_4$ AND PBu_3 IN ACETONE

M	ν(CO) (cm^{-1})
Cr	1991, 1931, 1902
Mo	1999, 1937, 1901
W	1996, 1929, 1896

by its air-sensitivity in solution. However, on one occasion addition of ether to the reaction mixture yielded red crystals, which were stable for several days in the air. The IR spectrum of this crystalline product was identical with that of the bulk reaction mixture (Table 1). More significantly, its field desorption (FD) mass spectrum characterized it unequivocally as the phosphonium adduct Ib. At low emitter currents the only peaks observed were those attributable to molecular $[M]^+$ and $[M+1]^+$ ions. At higher emitter currents other peaks were also observed consistent with the loss of PBu_3 (*m/e* 202) and $C_7H_7PBu_3$ (*m/e* 293). These results provide a further illustration of the value of FD mass spectra in identifying organometallic salts [4]. Although the tungsten adduct was not isolated, it is stable for several hours in solution.

Addition of excess tri-n-butylphosphine (ca. 5×10^{-2} *M*) to the reaction mixtures in Table 1 led to different results. No change in the IR spectrum occurred for the chromium case, in agreement with Hackett et al. [1]. However, with molybdenum the peaks due to Ib disappeared, being replaced by a single band at 1926 cm^{-1}. The peaks at 1926 cm^{-1} can be assigned to $[(PBu_3)_3Mo(CO)_3]$, which is the product reported by Graham at al. [3] the second band expected for this species at ca. 1835 cm^{-1} could not be observed due to absorption by the acetone solvent). In the case of tungsten, the peaks due to Ic again disappeared and were replaced by a single band at 1920 cm^{-1} assignable to $[(PBu_3)_3W(CO)_3]$. No IR evidence was obtained in any instance for the formation of carbonyl-displacement products. These results are summarised in Scheme 1 (M = Mo W).

$$[(C_7H_7)M(CO)_3]BF_4 + PBu_3 \xrightarrow{\text{acetone}} \underset{\text{(I)}}{[(C_7H_7PBu_3)M(CO)_3]BF_4} \xrightarrow[\text{acetone}]{\text{excess } PBu_3}$$

$$\underset{\text{(III)}}{[(PBu_3)_3M(CO)_3]} + [C_7H_7PBu_3]BF_4$$

Scheme 1

The uniform occurrence of eq. 1 as the first reaction between all $[(C_7H_7)M(CO)_3]^+$ cations and tri-n-butylphosphine (at low concentrations) is not surprising in view of recent kinetic results [5] showing the electrophilicity of the tropylium rings to be independent of the nature of the metal. The previous observation [2,3] of only carbonyl- or ring-displacement products from reaction of $[(C_7H_7)Mo(CO)_3]BF_4$ with phosphines no doubt arises from the high nucleophile concentrations and/or long reaction times employed. Under such conditions, nucleophilic attack at the metal is much more likely for molybdenum than for chromium substrates, rates generally decreasing in the order Mo > W >> Cr [6,7]. This also explains why in the present study conversion I → III only occurs for the molybdenum and tungsten complexes*.

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*Since this work was completed Dr. A. Salzer has kindly informed us of his similar studies of phosphine addition to [$(C_7H_7)M(CO)_3$]BF_4 (M = Mo, W) complexes (Abstr. Conf. Organometal. Chem., Venice, 1975; and Inorg. Chim. Acta, in press). His conclusions are similar to ours. However, his studies concentrated in triisopropylphosphine and he was unable to characterise the tri-n-butylphosphine adducts.