# Electrophilic Attack on Unsubstituted Phosphorus Units in Transition Metal Compounds: Synthesis and Characterization of the Methyltriphosphirene Unit Stabilized by Transition Metal–Ligand Fragments

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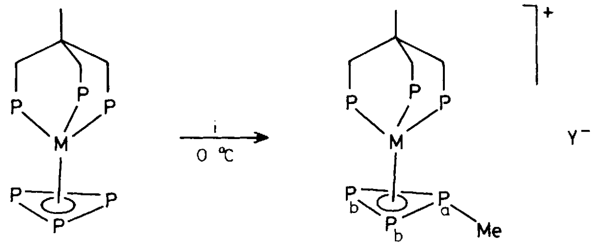
The reaction of trimethyloxonium tetrafluoroborate or methyl trifluoromethanesulphonate with the [(triphos)M($P_3$)] complexes [triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane; M = Co, Rh, or Ir] in which the triphosphirene ring is $\eta^3$-bonded to the metal, yields the compounds [(triphos)M($MeP_3$)]Y (Y = $BF_4$, $CF_3SO_3$) which contain the novel methyltriphosphirene unit $\eta^3$-linked to the M(triphos) moiety.

Transition metal compounds containing ligand units formed by unsubstituted p-block atoms are currently of great interest owing to both the unusual nature of the units, which may be stabilized under appropriate conditions, and the nature of the bonding within such units and between these and the transition metal atoms.[1] Phosphorus and arsenic atoms seem to be particularly suitable for the formation of such fragments linked to metal centres. In particular, by the reaction of small molecules containing group 5 atoms with appropriate transition metal–ligand moieties, compounds containing the *cyclo*-$E_3$,[2] -$E_5$[3] (E = P or As) and -$P_6$[4] units $\eta$-bound to the metal–ligand system have been obtained. The structural importance of the group 5 atom rings and the interest in the transition metal part of the molecules have overshadowed the fact that each unsubstituted group 5 atom is isoelectronic with a CH group. The $E_3$, $E_5$, and $P_6$ cyclic units are indeed formally analogous to unsaturated organic molecules so that they may be expected to exhibit similarities in reactivity to the latter. On the other hand, no electrophilic or nucleophilic activation of such co-ordinated units by organic reagents has been reported so far in spite of the fact that the presence of lone pair electrons on the group 5 atoms should make the inorganic units more reactive than the isoelectronic organic molecules.

We now report that the neutral [(triphos)M($P_3$)] complexes [triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane; M = Co, Rh, Ir] undergo electrophilic attack by methylating agents, yielding the compounds [(triphos)M($MeP_3$)]Y·$C_6H_6$ (Y = $BF_4$ or $CF_3SO_3$) in which the methyltriphosphirene ring is $\eta^3$-bound to the M(triphos) moiety.

[(triphos)M($P_3$)] (M = Co, Rh, or Ir) dissolved in methylene chloride was allowed to react at 0 °C with the stoicheiometric amount of trimethyloxonium tetrafluoroborate or methyl trifluoromethanesulphonate. The Co derivative reacted completely in *ca.* 2 h; longer reaction times (*ca.* 3 h) were needed for the Rh and Ir complexes. Red (Co) (**1**), orange (Rh) (**2**), and yellow (Ir) (**3**) compounds were obtained by adding benzene and concentrating the resulting solution. All manipulations were carried out under nitrogen and the solvents carefully purified prior to use. Yields were *ca.* 80% for all compounds.†



M = Co(**1**), Rh(**2**), Ir(**3**)
Y = $CF_3SO_3$, $BF_4$

**Scheme 1.** *Reagents:* i, $CF_3SO_3Me$ or [$Me_3O$]$BF_4$.

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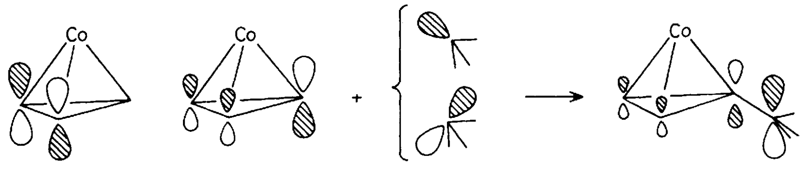
† C, H, Co (Rh or Ir), and P elemental analyses agree with the formula [(triphos)M($MeP_3$)]Y·$C_6H_6$ (Y = $BF_4$, $CF_3SO_3$); in dichloroethane solution the compounds behave as 1 : 1 electrolytes. The following $^1H$ and $^{31}P$ n.m.r. shifts refer to $CDCl_3$ solutions at room temperature relative to $SiMe_4$ and 85% $H_3PO_4$, respectively; positive shifts are to low frequency, *J* in Hz. $^1H$ signals of the triphos ligand and the benzene solvate molecule are not reported for they exhibit the expected chemical shift, and the intensities are in accordance with the proposed formulae. (**1**): $^1H$, $\delta$ 2.21 (d, 3H, Me), $^2J(H–P_a)$ 12; $^{31}P$ $\delta$ 32.9 (br., 3P, triphos), $-121.0$ (br. t, 1P, $P_a$), and $-342.2$ p.p.m. (br. d, 2P, $P_b$), $^1J(P_a–P_b)$ 362. (**2**): $^1H$, $\delta$ 1.34 (d, 3H, Me), $^2J(H–P_a)$ 13. (**3**): $^1H$, $\delta$ 1.36 (d, 3H, Me), $^2J(H–P_a)$ 14.



(4) (5) (6)

Scheme 2

The solid compounds decompose readily on exposure to air, but give stable dichloromethane or chloroform solutions under an inert atmosphere. The derivatives react, even under nitrogen, with solvents having nucleophilic groups like alcohols and ethers, giving rise to products whose nature is currently under investigation.

The structure of the [(triphos)Co(MeP$_3$)](BF$_4$)·C$_6$H$_6$ (**1**) compound has been established by a single crystal *X*-ray diffraction study.‡ The structure consists of [(triphos)-Co(MeP$_3$)]$^+$ cations, BF$^-{}_4$ anions, and solvate benzene molecules. The methyltriphosphirene unit is $\eta^3$-bonded to the cobalt atom (Figure 1), which is also co-ordinated by the three phosphorus atoms of the triphos ligand. The CoP$_3$ core, which had crystallographic threefold symmetry in the [(triphos)-Co(P$_3$)] parent compound[5] with 2.301(1) Å Co–P and 2.141(2) Å P–P distances, undergoes a notable distortion upon addition of the Me group; the Co–P(6) distance [2.16(1) Å], involving the substituted P atom, is much shorter than the other two Co–P distances [Co–P(4) 2.41(1), Co–P(5) 2.381(1) Å], and the P–P bonds formed by P(6) are shorter than the third P–P bond in the P$_3$ unit [P(4)–P(6) 2.08(2), P(5)–P(6) 2.08(2), P(4)–P(5) 2.17(2) Å].

The same structure may be assigned to the rhodium (**2**) and iridium (**3**) derivatives on the basis of elemental analyses, conductometric data, and $^1$H n.m.r. spectra.

The deformation undergone by the CoP$_3$ core may be attributed, on the basis of extended Hückel calculations, to the interactions (Scheme 2) of the HOMO and LUMO of the Me group with one component (**5**) of a doubly degenerate set of high-energy occupied orbitals of the [(triphos)Co(P$_3$)] parent. A decrease in antibonding interactions between the substituted P atom and the other two P atoms in the ring occurs (**6**), whereas the accompanying decrease in the small bonding interaction between the latter atoms leads to an overall increase of antibonding interactions between them since (**4**) is essentially unmodified by the methylation. Similarly, the trends in values of Co–P(P$_3$) overlap population match the observed trends in bond lengths.

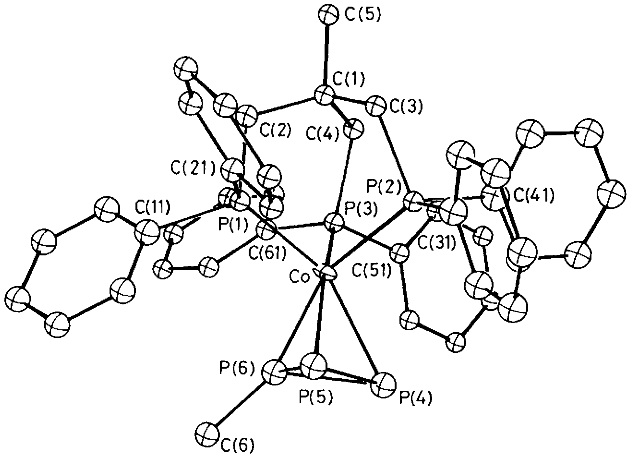


**Figure 1.** A view of the [(triphos)Co(MeP$_3$)]$^+$ cation with 20% probability ellipsoids. Only the first carbon atom of each phenyl group is labelled. Bond distances: P(6)–C(6), 1.78(3); P(4)–P(5), 2.17(2); P(4)–P(6), 2.08(2); P(5)–P(6), 2.08(2); Co–P(1), 2.20(1); Co–P(2), 2.22(1); Co–P(3), 2.21(1); Co–P(4), 2.41(1); Co–P(5), 2.38(1); Co–P(6), 2.16(1) Å. Bond angles: Co–P(6)–C(6), 157.5(1.11)°.

We believe that these results provide an unprecedented example of reactivity, which should be further investigated, of organic reagents towards substrates formed by bare main group atom fragments co-ordinated to a metal centre.

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‡ Crystals of [(triphos)Co(MeP$_3$)](BF$_4$)·C$_6$H$_6$ (**1**) were very small, and diffracted badly, yielding very few reflections. *Crystal data:* C$_{48}$H$_{48}$BCoF$_4$P$_6$, $M$ = 956.50, monoclinic, space group $P2_1/n$, $a$ = 17.58(1), $b$ = 19.92(1), $c$ = 13.35(1) Å, $\beta$ = 103.8(1)°, $U$ = 4540 Å$^3$, $Z$ = 4, $D_c$ = 1.40 g cm$^{-3}$, $\mu$(Mo-$K_\alpha$) = 6.33 cm$^{-1}$. Of a total 2062 independent reflections measured to $2\theta$ = 30° on a Philips PW 1100 diffractometer with graphite-monochromated Mo-$K_\alpha$ radiation, 703 [$I > 3\sigma(I)$] were considered to be 'observed' and used for structure solution and refinement. The structure was solved by heavy-atom methods and refined with anisotropic Co and a set of 11 overall isotropic thermal parameters for atoms forming phenyl rings or other groups. Phenyl groups were refined as rigid bodies and geometrical constraints were imposed on sets of chemically equivalent bonds, H atoms being introduced in calculated positions [C–H = 1.00 Å, $U$(H) = 1.2 $U$(C)]. The final $R$ was 0.079 [$R_w$ = 0.086, $w = 1/\sigma^2(F_o)$]. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.