Rapid Phosphorus–Carbon Bond Cleavage in Bis(diphenylphosphino)methane under Very Mild Conditions: a One-step Synthesis of μ-PPh_2, μ-$Ph_2PCH_2PPh_2$ Binuclear Co^I and Ni^I Carbonyls directly from Co^{II} and Ni^{II} Salts

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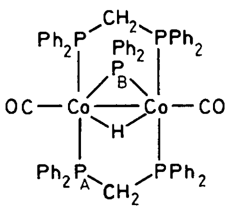
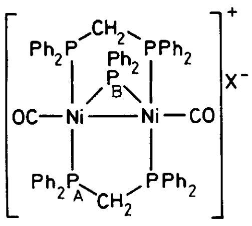
Co^{II} and Ni^{II} react rapidly with $NaBH_4$ in the presence of bis(diphenylphosphino)methane (dppm) under CO at or below (0 °C) room temperature to yield complexes of the types $Co_2(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-dppm})(CO)_4$, $Co_2(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-dppm})_2(CO)_2$, and $[Ni_2(\mu\text{-}PPh_2)(\mu\text{-dppm})_2(CO)_2]X$ ($X = Cl, BPh_4$).

An increasingly important route to phosphido-bridged bi- and poly-nuclear complexes involves a transition metal mediated P–C bond cleavage, normally under forcing conditions, in simple tertiary phosphine[1] (or, occasionally, bis- or poly-phosphine[2]) complexes. Recently, however, it has been reported that for certain di-iron carbonyl[3,4] and platinum chloride[5] complexes of bis(diphenylphosphino)methane (dppm),[3,5] and of other closely related structures containing the P–C–P linkage,[3,4] the formation of phosphido-bridged complexes occurs under unusually mild conditions [boiling tetrahydrofuran (THF)[3] or heptane,[4] NaOH/liq.NH_3 at −50 °C[5]] with both fragments resulting from P–C–P cleavage



(1)



(2)

remaining in the products. We report here examples of very rapid P–C bond cleavage in dppm, at or below room temperature, leading to the formation of phosphido-bridged Co^I or Ni^I binuclear carbonyl complexes in acceptable yields in a single experimental step directly from Co^{II} or Ni^{II} salts.

In recent studies of the room-temperature reactions of Co^{II} (ref. 6) and Ni^{II} (ref.7) salts with $NaBH_4$ (or $NaBH_3CN$) in the presence of dppm under CO, we have shown that a variety of, mainly, M^0/dppm/CO (M = metal) complexes containing bridging, chelating, or monoco-ordinated dppm can readily be synthesized with the nature of the product being determined primarily by the rate of addition of $NaBH_4$ (10—30 min). However, if the addition of $NaBH_4$ is carried out during 1 min or less, the reactions produce primarily binuclear Co^I or Ni^I μ-PPh_2 complexes. Thus, treatment of a mixture of $CoCl_2 \cdot 6H_2O$ and dppm in $EtOH/C_6H_6$ with $NaBH_4$ in EtOH, under a CO atmosphere at room temperature and with the reagents in a molar ratio of 1 : 2 : 3, yields† the complex (1) as the principal product. In a modification of the procedure, treatment of $CoCl_2 \cdot 6H_2O$ and dppm in $EtOH/C_6H_6$ (4 : 1) with $NaBH_4$ in EtOH (with the reactants in a ratio of 1 : 2.3 : 2.3) over 10 min followed by filtration and the passage of CO (90 min) through the brown filtrate yields, as a green precipitate, a mixture (2 : 5 by ^{31}P NMR integration) of the known[2a] $Co_2(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-dppm})(CO)_4$‡ and (1) separable by recrystallization from $CH_2Cl_2/EtOH$.

The hydrido phosphido complex (1) may also be prepared (33% after recrystallization from $CH_2Cl_2/EtOH$) when $Co_2(\mu\text{-dppm})_2(CO)_4$[6] is heated under reflux (3 h) in degassed toluene under H_2. The reaction is clean and ^{31}P examination of the reaction mixture shows that no detectable amounts of free Ph_2PMe (the most probable other product of dppm cleavage in the presence of H_2) are present.

Similar reactions with the $NiCl_2 \cdot 6H_2O/dppm/BH_4^-/CO$ system lead to the formation of (2) (a rare example of a cationic phosphido-bridged species) in good yield together with a variety of other products (^{31}P NMR), the presence of which makes the isolation of pure (2) (X = Cl or BPh_4) difficult. However, pure (2) can readily be prepared, as the BPh_4^- salt, in an unusual procedure expected originally to produce heterobimetallic M^0/dppm/CO complexes analogous to the binuclear Co systems already reported.[6] Indeed, a variation of this general procedure has already resulted in the formation of $CoRh(\mu\text{-dppm})_2(CO)_3$ in good yield.[8] Thus, treatment of the brown filtrate obtained from Co^{II}/dppm/BH_4^- reactions (referred to above) with $NiCl_2 \cdot 6H_2O$ prior to the passage of CO gives a black precipitate, ethanolic solutions of which yield (2) (X = BPh_4) upon treatment with $NaBPh_4$.§ This series of reactions also occurs readily at 0 °C.

A broader investigation with other transition metal salts is currently in progress as is a study of the mechanism of the P–C bond cleavage in dppm under these conditions.

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† Typical experimental details are: a solution of $CoCl_2 \cdot 6H_2O$ (0.883 g) and dppm (2.79 g) in degassed $EtOH/C_6H_6$ (1 : 1, 30 ml) was treated with CO gas for 5 min, $NaBH_4$ (0.400 g) in degassed EtOH (30 ml) was added dropwise over 1 min, and the mixture was stirred under CO for 30 min. The initial dark green solid formed (0.960 g), shown by ^{31}P NMR integration to be approximately a 7 : 3 mixture of (1) and dppm monoxide [*i.e., ca.* 32% yield of (1)], was recrystallized from $CH_2Cl_2/EtOH$ to give analytically pure (1) (10—20% yield over several experiments). Satisfactory chemical analyses for this and the other complexes reported herein were obtained. Later crops from the crude reaction mother liquor contain increasing amounts of the known[6] $Co_2(\mu\text{-dppm})_2(CO)_4$. *Spectroscopic data* for (1): IR (Nujol), ν_{CO} 1921 cm^{-1}; ^1H NMR ($CHCl_3$, D_2O lock), $\delta_{Co\text{-}H}$ −17.75 ($J_{P_AH} = J_{P_BH}$ = 29.2 Hz); ^{31}P NMR, δ_{P_A} 47.6, δ_{P_B} 215.6 ($J_{P_AP_B}$ 54 Hz).

‡ ^1H NMR, $\delta_{Co\text{-}H}$ −8.49 (J_{P_AH} 33.3, J_{P_BH} 64.2 Hz); ^{31}P NMR, δ_{P_A} 62.0, δ_{P_B} 224.1 ($J_{P_AP_B}$ 93.2 Hz).

§ The salt $CoCl_2 \cdot 6H_2O$ (0.55 g) in EtOH (40 ml) was mixed with dppm (2.04 g) in toluene (10 ml), $NaBH_4$ (0.2 g) in EtOH (15 ml) was added over 15 min, and the resulting brown suspension was filtered. To the filtrate was added solid $NiCl_2 \cdot 6H_2O$ (0.55 g) and CO was passed for 90 min during which time the solution became purple. Hexane (40 ml) was added and the mixture was chilled (freezer) for 96 h. The resulting black solid was dissolved in EtOH (85 ml) and solid $NaBPh_4$ (0.78 g) was added to yield crude (2) (X = BPh_4) as a purple solid which was redissolved in CH_2Cl_2 (7 ml) to which EtOH (35 ml) was added. After 48 h, pure (2) (X = BPh_4) (19% yield) crystallized. IR, ν_{CO} 1996 cm^{-1}; ^{31}P NMR, δ_{P_A} 15.6, δ_{P_B} 239.8 ($J_{P_AP_B}$ 57.5 Hz).