## Novel Routes to Functionalized Diphosphine- $M(CO)_4$ Complexes (M = W, Mo, or Cr)

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Complexes of type  $[(OC)_4M{(Ph_2P)_2C=CH_2}]$  undergo Michael type additions with a range of amines, including optically active amines, hydrazines, acetylides, and dichlorocarbene and the products can be used for further syntheses.

Although tertiary phosphines are important ligands in chemistry, relatively little has been done with functionalized phosphines, partly because of difficulties in synthesis. We have reported briefly that the complex  $[(OC)_4W\{(Ph_2P)_2-C=CH_2\}]$  undergoes Michael type addition with pyrrolidine to give  $[(OC)_4W\{(Ph_2P)_2CHCH_2NC_4H_8\}]^1$  and we now report that such additions are extensive and can be used as the basis of a wide range of syntheses of complexes containing functionalized diphosphines (see Scheme 1).† We find that the free diphosphine,  $(Ph_2P)_2C=CH_2$ ,<sup>2</sup> does not react with amines

 $^{\dagger}$  The complexes described in this communication have been characterized by elemental analysis {C, H, N, and Cu in the case of (5)} and by  $^{1}H$ ,  $^{1}H{}^{31}P$ , and  $^{31}P{}^{1}H{}$  n.m.r. and i.r. spectroscopy.



Scheme 1. For simplicity, reactions are shown for tungsten complexes: several reactions were also done with the analogous molybdenum or chromium complexes (1b) or (1c). i,  $N_2H_4$ · $H_2O$ , 5 min at *ca*. 60 °C;  $H_2NNHMe$  or  $H_2NNMe_2$ , 18 h, 90 °C; ii, dissolution in acetone at 20 °C; iii, salicylaldehyde, 80 °C, 1 h; iv, Cu(OAc)<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub>-EtOH, 1 min, 20 °C; v, PhCHMeNH<sub>2</sub> (*R*- or *S*-), 16 h, 20 °C; vi, CH<sub>2</sub>=CHCH<sub>2</sub>NH<sub>2</sub>, 2 min, 40 °C; CH<sub>2</sub>=CHCH<sub>2</sub>NHMe, 16 h, 20 °C; vii, NaCH(CO<sub>2</sub>Et)<sub>2</sub> in THF, 16 h, 20 °C; viii, LiC=CR + TMEDA in THF, 18 h, 20 °C; ix, Bu<sup>1</sup>OK in propan-2-ol, 90 min, 80 °C, then acidify; x, CHCl<sub>3</sub> + 40% aqueous KOH, 55 °C, 2 h + phase-transfer catalyst; xi, Ph<sub>2</sub>PH + Bu<sup>1</sup>OK in THF, 50 °C, 3.5 h.

or hydrazine but complexation, even to a relatively weakly electron withdrawing group,  $(OC)_4M$  (M = W, Mo, or Cr), is sufficient to render C=CH<sub>2</sub> reactive towards Michael type additions.

A toluene solution of the tungsten complex  $(1a)^3$  when warmed and shaken with an excess of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O gives after ca. 5 min, a 90% yield of the yellow, crystalline substituted hydrazine (2a). The corresponding Mo and Cr complexes reacted similarly. When a toluene solution of (1a) was heated with an excess of methylhydrazine or N, N-dimethylhydrazine (90 °C, 18 h) the corresponding di- and tri-substituted hydrazines (2b) and (2c) were isolated in 65 and 82% yields; probably shorter reaction times could be used. Alkyl- and aryl-hydrazines have a very extensive chemistry and we find that (2a) readily undergoes high yielding condensation reactions. Thus on dissolution in cold acetone, the hydrazone (3)forms and can readily be isolated (91% yield) and when heated with a slight (20%) excess of salicylaldehyde in boiling benzene for 1 h the yellow, crystalline hydrazone (4) was isolated in >90% yield. Salicylimines and related molecules are very good chelating ligands and we find that the hydrazone (4), when treated with the equivalent amount of copper(II)acetate rapidly gives the brown, crystalline ditungsten-copper complex (5).

There is a lot of interest in chiral phosphines in synthesis. Such phosphines are generally difficult to make. We find that the readily available amines, R- and S- $\alpha$ -methylbenzylamine, add to (1a) to give the chiral adducts (6a) and (6b) respectively in >80% isolated yield (reaction conditions 20 °C, 16 h). Benzylamine or 4-methoxybenzylamine similarly add to (1a) in isolated yields of typically 80-90%. We also find that the vinylidene-diphosphine complex (1a) when warmed with allylamine dissolves and after ca. 2 min the crystalline adduct (7a) separates and can be isolated in 83% yield. N-Methylallylamine reacts similarly with (1a) but more slowly (16 h, 20 °C in toluene solution) to give (7b). It has been shown that N, N-dimethylallylamine reacts with Na<sub>2</sub>PdCl<sub>4</sub> in MeOH to give  $[\dot{P}d_2\{NMe_2CH_2CH(OMe)\dot{C}H_2\}_2(\mu-Cl)_2]^4$  We find that (7b) reacts rapidly with  $Na_2PdCl_4$  in  $CH_2Cl_2$ -MeOH to give an intensely red solution, which we are investigating.

We have also studied the action of some carbon nucleophiles on (1a), which reacts with NaCH(CO<sub>2</sub>Et)<sub>2</sub> in tetrahydrofuran (THF) to give the adduct (8) (after acidification). We found that (1a) was recovered unchanged after prolonged (16 h) treatment with LiC=CPh in THF but in the presence of Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> (TMEDA) to solvate the lithium, smooth Michael type addition occurred and the hoped for adduct (9a) was obtained in >90% yield as orange needles; ment, a well-established reaction of acetylenes. When (9a) was heated with Bu<sup>t</sup>OK in refluxing propan-2-ol an intensely green solution formed which when cooled and acidified gave the hoped for deep red crystalline diene-diphosphine complex (10a) in 91% isolated yield. We have determined the crystal structure of (10a). The p-tolyl analogue (10b) was prepared similarly. We also find that when a chloroform solution of (1a) is heated (55 °C) and stirred with 40% aqueous KOH, using PhCH<sub>2</sub>NMe<sub>3</sub>Cl as phase-transfer catalyst, the yellow crystalline dichloro-carbene adduct (11) was readily isolated in 78% vield. The Mo and Cr analogues were prepared similarly. We have determined the crystal structure of (11) and confirmed the presence of the cyclopropane ring. Recently the cyclopropyl-diphosphine (Ph<sub>2</sub>P)<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub> has been prepared by treating (Ph<sub>2</sub>P)<sub>2</sub>C=CH<sub>2</sub> with Me<sub>2</sub>SO(=CH<sub>2</sub>).<sup>5</sup> We

also find that (1a) reacts rapidly with Ph<sub>2</sub>PH in the presence of ButOK to give the triphosphine complex (12) in 36% yield.

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