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Preliminary communication

Stabilization of the bis(diphenylphosphino)methanide ion by bridging dirhenium octacarbonyl: $[Li(THF)_4][Re_2(CO)_8(Ph_2PCHPPh_2)]$

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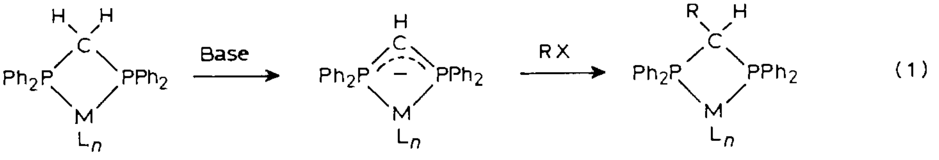
Abstract

The anion of $[Li(THF)_4][Re_2(CO)_8(Ph_2PCHPPh_2)]$ (**1**) is formed cleanly by treatment of $Re_2(CO)_8(Ph_2PCH_2PPh_2)$ with $LiAlH_4$ in tetrahydrofuran (54% yield). Anion **1** is remarkably stable toward all organic electrophiles examined. Whereas protons are added and removed reversibly, **1** is stable to treatment with MeI, Me_3SiCl, Me_3SiCH_2Cl or Ph_2PCl, even under forcing conditions. This behavior sharply contrasts the high reactivity of other mononuclear $(Ph_2PCHPPh_2)ML_x$ complexes.

Deprotonation of chelating bis(diphenylphosphino)methane (dppm) in mononuclear complexes occurs with a variety of bases and the resulting anions are readily alkylated with electrophiles [1]. This is the most important route to functionalizing dppm (eq. 1) [2].



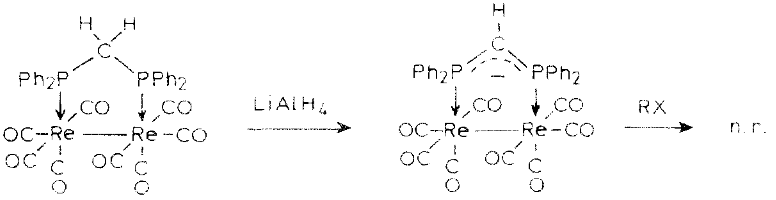
(1)

(M = Cr, Mo, W, Pd, Pt)

The dppm ligand plays an equally important role for binding metal dimers together and promoting binuclear reactions [3]. It is surprising that the deprotonation/alkylation sequence above (eq. 1) has not been extended to these dppm-bridged metal dimers.

We sought to investigate the reactions of bases with the dppm-bridged carbonyl dirhenium complex, $Re_2(CO)_8$(dppm) [4], with the aim of isolating a dppm methanide anion of a metal dimer which could be further functionalized. We now report that of the several bases examined, only $LiAlH_4$ cleanly deprotonates the dppm methylene yielding the dirhenium methanide anion, $Re_2(CO)_8(Ph_2PCHPPh_2)^-$ (**1**). During alkylation studies however, this anion proved to be completely stable to reaction with a variety of electrophiles even under forcing conditions. This is in sharp contrast to the known facile reactivity of mononuclear dppm methanide complexes.

Lithium aluminum hydride (50 mg, 1.3 mmol) was added to a dry tetrahydrofuran (THF) solution (10 ml) of $Re_2(CO)_8$(dppm) (100 mg, 0.102 mmol) under N_2 and stirred for 3 h. The solvent was removed under reduced pressure and the resulting grey residue was extracted into toluene. The yellow suspension was filtered and the solvent was removed under reduced pressure leaving **1** as a yellow microcrystalline solid (70 mg, 54%) [5 *]. Benzene-d_6 solutions of **1** consistently contain four equivalents of THF per mole of the anion as determined by integration of the THF resonances in the ^{1}H NMR spectra. The spectroscopic properties of **1** are consistent with a structure that is analogous to that of the parent complex, $Re_2(CO)_8$(dppm). The IR(ν(CO)) spectra of $Re_2(CO)_8$(dppm) and **1**, shown in Fig. 1, emphasizes the similarity of the infrared patterns in the carbonyl region indicating that both possess the same symmetry. The negative charge on **1** shifts the IR absorptions to lower frequencies. The NMR data are consistent with a metal-bridging $Ph_2PCHPPh_2$ group with the negative charge delocalized over the P–C–P linkage [5]. Treating **1** with H_2O readily regenerates the starting material while treatment with D_2O gives the d_1 complex.



(**1**)

(2)

Anion **1** was found to be inert toward all other electrophiles studied: MeI, Me_3SiCl, Me_3SiCH_2Cl and Ph_2PCl. ^{1}H NMR scale investigations involving addition of Me_3SiCH_2Cl to a saturated THF-d_8 solution of **1** revealed only resonances attributable to unreacted electrophile and unreacted anion even after 48 h. The reactants were still observed unchanged in a sealed NMR tube after heating for 15 h at 85 °C! The analogous NMR scale reaction with Ph_2PCl as the electrophile was similarly monitored by ^{31}P NMR spectroscopy. Resonances assignable to dirhenium coordinated tris(diphenylphosphino)methane (tripod) were not observed [6 *].

The coexistence of **1** with electrophiles such as Me_3SiCH_2Cl in solution is particularly remarkable in light of the facile alkylations of mononuclear dppm complexes. Only rearranged products are observed from the deprotonation of dppm dimers of iron or platinum [7]. The only other bimetallic deprotonated dppm complexes are gold dimers $[Au_2(Ph_2PCHPPh_2)L_2]$ [8] and rhodium dimers $Rh_2(\mu$-

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* Reference numbers with asterisks indicate notes in the list of references.

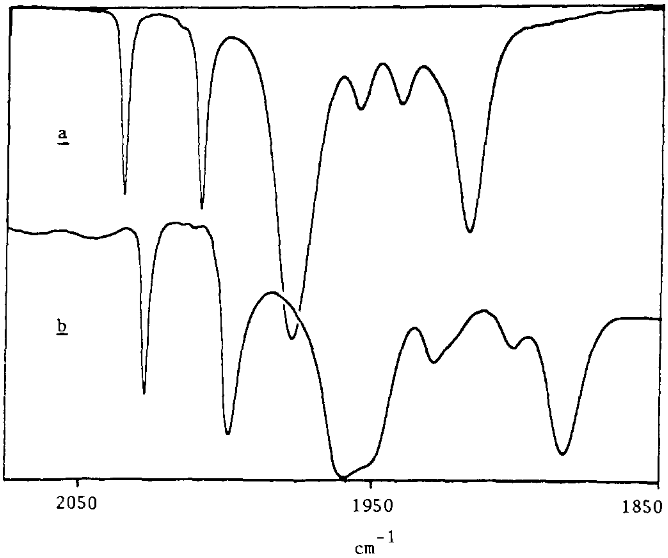

Fig. 1. IR(ν(CO), THF) of (a) $Re_2(CO)_8$dppm and (b) **1**; illustrating the similarity of the patterns and the shift to lower frequencies of the absorbtions of **1** vs. those of $Re_2(CO)_8$dppm.

NHR)$(CO)_2$(dppm)$(Ph_2PCHPPh_2)$ [9] whose reactivity with electrophiles has not been reported.

The stability of **1** towards electrophiles presumably results from both steric congestion and charge delocalization about the methanide carbon. The steric requirements of the Ph groups in mononuclear dppm complexes have been found to insulate chemically the adjacent metal center from attack and can dictate further molecular structure [10]. This is clearly indicated in recent studies of Sn [11,12] and Pb [12] dppm methanide complexes. By bridging $Ph_2PCHPPh_2^-$ across the Re–Re bond in **1**, the Ph groups are forced to bend toward the methanide carbon relative to the structures of mononuclear dppm methanide complexes. The methanide carbon would thus be effectively protected from electrophiles other than H^+. The X-ray structures of two mononuclear dppm methanide complexes and a rhenium dppm dimer are in agreement with this. The complex $Pt(Ph_2PCHPPh_2)_2$ has a P–C–P bond angle of 99.4(1)° [13] and $[PtCl(PEt_3)(Ph_2PCHPPh_2)]$ has a P–C–P angle of 98.6(5)° [14]. In contrast, the neutral dimer $Re_2(CO)_6$(dppm)(μ-H)(μ-OH) has an open P–C–P angle of 112.1(4)° [4]. The more open P–C–P angle in the rhenium dimer relative to those in the platinum complexes apparently results in sufficient bending of the Ph_2P moieties toward the methanide carbon to block electrophilic attack.

Anion **1** is electronically stabilized through the delocalization of the negative charge to the phosphorus atoms, and also by the electron withdrawing effect of the complexed rhenium. Binding metals to the phosphorus in dppm is reported to increase the acidity of the methylene protons [15].

This stabilizing phenomenon may be general for the many bridging dppm complexes known, but has not yet been reported. The described behaviour of this dppm methanide metal dimer is similar to that of organic hindered bases.

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5 ^{1}H NMR (100 MHz, $SiMe_4$, C_6D_6): δ 8.12 (m, 4, C_6H_5), 7.00 (m, 16, C_6H_5), 3.76 (t, 1, J(PH) 3.0 Hz, CH), 3.22 (m, 16, THF), 1.24 (m, 16, THF) ppm. $^{31}P\{^1H\}$ NMR (40.3 MHz, from ext. PPh_3 at δ −6.0 ppm, C_6D_6): δ −9.63 (s) ppm. IR (cm^{-1}, THF, ν(CO)): 2055m, 1998m, 1959s, 1927w, 1901w, 1884m.

6 We have synthesized the tripod complex, $Re_2(CO)_8[HC(PPH_2)_3]$, by an alternate route: $^{31}P\{^1H\}$ NMR (C_6D_6): δ 19.9 (d, 2, J(PP) 23 Hz), 4.4 (t, 1) ppm.

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