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Reactivity of bis(cyclopentadienyl)niobium and bis(cyclopentadienyl)tantalum trihydride towards bis(diorganosphosphino)alkanes $R_2P(CH_2)_nPR_2$ ($R \equiv Ph$, $n = 1, 2$ or 3; $R \equiv Me$, $n = 1$ or 2): synthesis of bimetallic dibridged complexes $[Cp_2M(\mu\text{-}H)(\mu\text{-diphosphine})M'(CO)_4]$ ($M \equiv Nb$ or Ta; $M' \equiv Cr$, Mo or W)

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Abstract

The trihydrides $[Cp_2MH_3]$ ($M \equiv Nb$ or Ta) react with diphosphines $R_2P(CH_2)_nPR_2$ ($R \equiv Me$ or Ph, $n = 1$ or 2) affording the monohydrides $[Cp_2M(H)\{R_2P(CH_2)_nPR_2\}]$. The bimetallic dihydride $[\{Cp_2NbH\}_2(\mu\text{-dppp})]$ ($dppp \equiv Ph_2P(CH_2)_3PPh_2$) is obtained by reaction of dppp with $[Cp_2NbH_3]$. The complexes $[Cp_2M(H)(diphosphine)]$ ($M \equiv Nb$ or Ta) are able to bind $M'(CO)_4$ fragments ($M' \equiv Cr$, Mo or W) and lead to the dibridged complexes $[Cp_2M(\mu\text{-}H)(\mu\text{-diphosphine})M'(CO)_4]$.

Keywords: Niobium; Tantalum; Hydrides; Diphosphines; Binuclear species

1. Introduction

Numerous bimetallic systems utilize diphosphines as bidentate ligands and many studies and applications have been performed with this type of organometallic complex. In the most cases, the diphosphine links two similar metals [1] but heterobimetallic systems [2] attract considerable interest in view of their potential in catalytic processes. Great attention is focused on the development of early–late transition metal combinations, since new reactivity patterns arising from cooperative effects may be expected with such bimetallic structures.

In our work on the synthesis and characterization of new heterobimetallic systems, we are interested in the application of diphosphines as bridging ligands for niobocene or tantalocene units with Group 6 metal moieties.

In this paper, we report the synthesis of a new class of functionalized metalloligands $Cp_2M(H)$(diphosphine) (diphosphine = $Ph_2PCH_2PPh_2$ (dppm), $PPh_2(CH_2)_2PPh_2$ (dppe), $Ph_2P(CH_2)_3PPh_2$ (dppp), $Me_2PCH_2PMe_2$ (dmpm) or $Me_2P(CH_2)_2PMe_2$ (dmpe) and their use as precursors of heterobimetallic dibridged complexes $[Cp_2M(\mu\text{-}H)(\mu\text{-diphosphine})M'(CO)_4]$ (M = Nb or Ta; M' = Cr, Mo or W).

2. Results and discussion

Complexes **1–5** were prepared from the trihydrides $[Cp_2MH_3]$ (M = Nb or Ta) by thermal displacement of dihydrogen in presence of one equivalent of diphosphine according to the usual synthesis procedure of complexes $[Cp_2M(H)PR_3]$ [3]. The reaction occurs at

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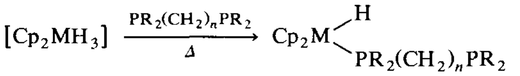
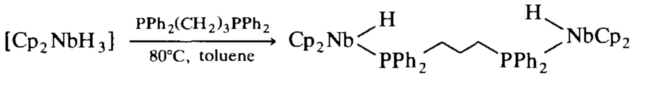
80°C with niobocene trihydride but the tantalum complex needs a higher temperature (130°C):



Complex	n	M	R
1	1	Nb	Ph
2	1	Nb	Me
2′	1	Ta	Me
3	2	Nb	Ph
4	2	Nb	Me
4′	2	Ta	Me



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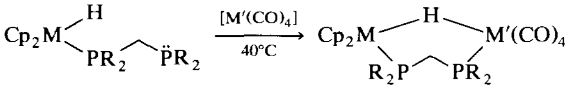
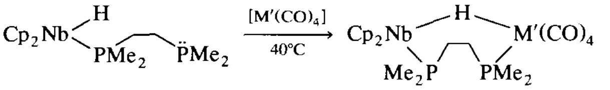
Surprisingly, the expected tantalum complexes were not formed with the phenyldiphosphines and the reaction gave the known tantalum dimer [{Cp_2TaH}$_2$] as the sole identified product [4]. With dppp, the niobocene trihydride leads to the bimetallic complex **5** whatever the reactant ratio. The presumed mononuclear intermediate was not detected. Both steric and electronic considerations can be advanced to account for the lack of the formation of such bimetallic complexes when other diphophines were used. For example, a critical distance between the two phosphorus coordination sites is required for minimizing the severe steric hindrance of two bulky Cp_2NbH entities. In addition it has been shown recently [5] that monoprotonation or monocomplexation by a Lewis-acid organometallic fragment on a bidentate phosphine greatly affects the basicity (determined by protonation enthalpy values of the dangling phosphorus atom. A significant decrease in the base character due to electron-withdrawing effects is observed with the ligands $R_2P(CH_2)_nPR_2$ with ($n = 1$, 2 or 3). However, there is little change in basicity under similar circumstances when $n = 5$ and 6. There is no proof of whether a steric or electronic effect is predominant in the failure to obtain bimetallic structures with a short-alkyl-chain ligand ($n = 1$ or 2).

All the complexes are very soluble in toluene, tetrahydrofuran (THF) and acetone and moderately soluble in hydrocarbon solvents. They were well characterized by their ^1H and ^{31}P NMR data. The hydride resonances fall in the range from -7 to -10 ppm and appear as doublets with a ^2J(P–H) value of about 21 Hz for tantalum complexes and 29 Hz for niobium complexes. The ^{31}P NMR data confirm the presence of a "free" phosphine group since two distinct resonances are observed: a downfield doublet assigned to the metal-bonded phosphorus atom and a more shielded signal for the terminal phosphorus, with a chemical shift very close to that of the free diphosphine. Coordination results in a downfield shift of about 80 ppm for niobium and 40 ppm for tantalum. The symmetrical structure of **5** is shown by the observation of a single ^{31}P resonance.

Treatment of metalloligands with [$M'(CO)_5$(THF)] ($M' \equiv$ Cr, Mo or W) does not result in the formation of the expected binuclear complexes [$Cp_2M(H)(\mu$-$PR_2(CH_2)_nPR_2)M'(CO)_5$] ($M \equiv$ Nb or Ta; $M' \equiv$ Cr, Mo or W; $n = 1$ or 2; $R \equiv$ Me or Ph) but NMR monitoring of the reaction mixture suggests the presence in small amount of μ-H bimetallic bridged complexes. These complexes are obtained with fairly good yield starting from [$M'(CO)_4$(norbornadiene) or [$M'(CO)_4$(piperidine)$_2$].



Complex	M	M′	R
6a	Nb	Cr	Ph
6b	Nb	Mo	Ph
6c	Nb	W	Ph
7a	Nb	Cr	Me
7b	Nb	Mo	Me
7c	Nb	W	Me
7′a	Ta	Cr	Me
7′b	Ta	Mo	Me
7′c	Ta	W	Me



Complex	M′
8a	Cr
8b	Mo
8c	W

The reaction proceeds smoothly and can be monitored in the CO absorption region by IR spectroscopy. The initial red solution turns deep green by the end of the reaction. The μ-diphosphine μ-H heterobimetallic complexes are isolated after chromatography on silica gel.

Again we have observed unexpected behaviour with tantalum derivatives, since no reaction occurs with [Cp_2TaH(dmpe)] (**4′**).

All the complexes shown characteristic IR pattern of an $M'(CO)_4$ moiety. In the ^1H NMR spectra, the high field resonances of hydrides (from -18 to -23 ppm) indicate hydride bridges [6]. For niobium derivatives, the signals appear are very broad singlets ($\Delta\nu_{1/2} \approx 30$ Hz) or ill-defined triplets ($J \approx 10$–15 Hz) and therefore suggest coupling to both phosphorus nuclei. In contrast a well-resolved doublet is observed ($J \approx 5$ Hz) with **7′a**–**7′c** showing coupling to only one P nucleus. This coupling is probably due to the tantalum-bonded phosphorus nucleus, because it can be assumed, at least in **7′b** and **7′c**, that the hydride lies nearer to the Group 5 element [7]. Two distinct resonance signals are found in the ^{31}P NMR spectra, arising from the two nuclei bonded to niobium or tantalum and to M′ respectively. The former is the more deshielded and remains invariant whatever the nature of M′. For the latter, an increased upfield shift is observed when going from Cr to W [8].

Work is in progress to test the reactivity of these binuclear complexes, mainly to determine the behaviour of the hydride bridge towards donors.

3. Experimental section

3.1. General considerations

All reactions were performed in Schlenk-type flasks under argon. Solvents (Merck) were dried and distilled under argon, over sodium benzophenone complex. $[Cr(CO)_4(\text{nobornadiene})]$ [9] and $[M'(CO)_4(\text{piperidine})_2]$ (M′ ≡ Mo or W) [10] were prepared according to literature procedures; dppm, dppe, dppp, dmpm and dmpe (Strem) were used without further purification.

NMR spectra were recorded on a Bruker AC 200 spectrometer at 200 MHz. IR spectra were obtained on a Nicolet 205 IR-FT spectrometer. Elemental analyses (C and H) were performed by the Service de Microanalyse du CNRS. Mass spectroscopy (MS) was recorded on a Kratos Concept 32 S spectrometer.

3.2. Synthesis

3.2.1. Preparation of $[Cp_2NbH(dppm)]$ (1)

$[Cp_2NbH_3]$ (0.50 g; 2.21 mmol) and dppm (0.85 g; 2.21 mmol) were allowed to react in toluene (30 ml) at 80°C for 2 h. The mixture turned deep red, which indicated the formation of $[Cp_2NbH(dppm)]$ (**1**). The solvent was evaporated to dryness under reduced pressure. The resulting solid was extracted with pentane (2 × 15 ml). A red powder of **1** (1.01 g; 75%) was obtained after removal of organic solvent. Anal. Found: C, 68.73; H, 5.34. $C_{35}H_{33}NbP_2$ Calc.: C, 69.08; H, 5.46%. ^1H NMR tetramethyl silane (TMS); C_6D_6): δ 4.48 (d, J(Cp–P) = 2.0 Hz, Cp); 3.33 (dd, $J(CH_2\text{–}P)$ = 3.0 Hz, $J(CH_2\text{–}P)$ = 6.0 Hz, $-CH_2-$); 6.90–7.90 (m, Ph); −7.14 (d, J(P–H) = 28.0 Hz, H). ^{31}P NMR (H_3PO_4; C_6D_6): δ 70.2 (broad); −26.3 (d, J(P–P) = 59.0 Hz).

3.2.2. Preparation of $[Cp_2NbH(dmpm)]$ (2)

To a solution of $[Cp_2NbH_3]$ (0.50 g; 2.21 mmol) in 30 ml of toluene was added dmpm (0.30 g; 2.21 mmol); this solution was stirred at 80°C for 2 h. Toluene was removed under vacuum and pentane was added to the residue. The solvent was evaporated to dryness yielding a red pyrophoric powder of **2′** (0.56 g; 70%). Anal. Found: C, 46.60; H, 6.85. $C_{15}H_{25}NbP_2$ Calc.: C, 50.02; H, 7.00%. ^1H NMR (TMS; CD_3COCD_3): δ 4.53 (d, J(Cp–P) = 1.9 Hz, Cp); 1.79 (dd, $J(CH_2\text{–}P)$ = 2.8 Hz, $J(CH_2\text{–}P)$ = 6.0 Hz, $-CH_2-$); 1.37 (d, J(Me–P) = 6.8 Hz, Me); 1.09 (d, J(Me–P) = 2.9 Hz, Me); −8.32 (d, J(P–H) = 29.0 Hz, H). ^{31}P NMR (H_3PO_4; CD_3COCD_3): δ 26.5 (broad); −55.8 (d, J(P–P) = 46.0 Hz).

3.2.3. Preparation of $[Cp_2NbH(dppe)]$ (3)

The procedure was the same as for **2**. The yield is 63%. ^1H NMR (TMS; C_6D_6): δ 4.39 (d, J(Cp–P) = 1.9 Hz, Cp); 2.41 (m, $-CH_2-$); 7.35–7.69 (m, Ph); −7.23 (d, J(P–H) = 27.0 Hz, H). ^{31}P NMR (H_3PO_4; C_6D_6): δ 74.0 (broad); −15.0 (s).

3.2.4. Preparation of $[Cp_2NbH(dmpe)]$ (4)

This complex was prepared in a manner analogous to **2** with a yield of 70%. Anal. Found: C, 48.28; H, 7.18. $C_{16}H_{27}NbP_2$ Calc.: C, 51.35; H, 7.27%. ^1H NMR (TMS; CD_3COCD_3): δ 4.50 (d, J(Cp–P) = 2.5 Hz, Cp); 1.51 (m, $-CH_2-$); 1.27 (d, J(Me–P) = 6.6 Hz, Me); 0.98 (d, J(Me–P) = 2.6 Hz, Me); −8.26 (d, J(P–H) = 28.0 Hz, H). ^{31}P NMR (H_3PO_4; CD_3COCD_3): δ 31.5 (broad); −45.3 (d, J(P–P) = 25.0 Hz).

3.2.5. Preparation of $[\{Cp_2NbH\}_2(\mu\text{-dppp})]$ (5)

$[Cp_2NbH_3]$ (0.45 g; 2.00 mmol) and dppp (0.40 g; 1.00 mmol) were allowed to react at 80°C in toluene (20 ml) for 2 h. The solvent was evaporated under reduced pressure and the resulting solid was extracted with pentane (2 × 15 ml). The solvent was evaporated to dryness under reduced pressure affording a brown powder of **5** (0.51 g; 60%). Anal. Found: C, 66.60; H, 5.62. $C_{47}H_{48}Nb_2P_2$ Calc.: C, 66.88; H, 5.92%. ^1H NMR (TMS; C_6D_6): δ 4.40 (d, J(Cp–P) = 2.0 Hz, Cp); 1.62 (m, $-CH_2-$); 1.91 (m, $-CH_2-$); 6.90–7.70 (m, Ph); −7.34 (d, J(P–H) = 27.0 Hz, H). ^{31}P NMR (H_3PO_4; C_6D_6): δ 69.0 (broad).

3.2.6. Reaction of $[Cp_2TaH_3]$ with dmpm (2′)

$[Cp_2TaH_3]$ (0.50 g; 1.59 mmol) and dmpm (0.22 g; 1.59 mmol) were stirred at 140°C in decane (20 ml) for 2 h. A red solution was obtained, showing the formation of $[Cp_2TaH(dmpm)]$ (**2′**). After evaporation of the solvent, pentane (20 ml) was added to the residue. Insoluble materials were filtered off. The resulting solution was taken to dryness to give an orange powder of $[Cp_2TaH(dmpm)]$ (0.46 g; 65%). ^1H NMR (TMS; CD_3COCD_3): δ 4.42 (d, J(Cp–P) = 1.3 Hz, Cp); 1.84 (dd, $J(CH_2\text{–}P)$ = 2.8 Hz, $J(CH_2\text{–}P)$ = 6.6 Hz, $-CH_2-$); 1.48 (d, J(Me–P) = 6.9 Hz, Me); 1.10 (d, J(Me–P) = 3.1 Hz, Me); −9.87 (d, J(P–H) = 21 Hz, H). ^{31}P NMR (H_3PO_4; CD_3COCD_3): δ −12.5 (d, J(P–P) = 43.0 Hz), −55.6 (d, J(P–P) = 44.0 Hz).

3.2.7. Reaction of [Cp_2TaH_3 with dmpe] (4′)

The procedure is similar to that detailed above for **2′** (yield, 60%). MS (electron impact (EI), 70 eV): *m/z* (%) 462 (4.3) $[M]^+$, 312 (14.4) $[Cp_2TaH]^+$, 57 (100). ^1H NMR (TMS; CD_3COCD_3): δ 4.39 (d, *J*(Cp–P) = 2.1 Hz, Cp); 1.54 (m, $-CH_2-$); 1.38 (d, *J*(Me–P) = 7.1 Hz, Me); 0.98 (d, *J*(Me–P) = 2.3 Hz, Me) −9.91 (d, *J*(P–H) = 21.0 Hz, H). ^{31}P NMR (H_3PO_4; CD_3COCD_3): or −1.3 (broad); −45.3 (d, *J*(P–P) = 25.0 Hz).

3.2.8. Reaction of [Cp_2NbH(dppm)] with [$M'(CO)_4L_2$] (M′ ≡ Cr, Mo or W; L_2 = norbornadiene or (piperidine)$_2$] (6a–6c)

To a THF solution (20 ml) of [Cp_2NbH(dppm)] (0.50 g; 0.82 mmol) was added one equivalent of [$Cr(CO)_4$(norbornadiene) or [$M'(CO)_4(piperidine)_2$] (M′ ≡ Mo or W). The mixture was stirred at 40°C for 1 h. The solvent was removed in vacuo, and the solid was washed with pentane (10 ml) and dried in vacuo. The solid, dissolved in toluene (5 ml), was chromatographed over a silica gel (70–230 mesh) column. Impurities were first eliminated by eluting with toluene, and **6a–6c** were recovered with a mixture of toluene–THF (10 : 1). The solution was evaporated off, leading a deep green powder. The yield was 30% in the molybdenum case and 60% in the chromium and tungsten cases.

6a: IR (THF): ν(CO) 1995 (s), 1933 (vs), 1875 (vs), 1849 (vs) cm^{-1}. ^1H NMR (TMS; CD_3COCD_3): δ 4.87 (d, *J*(Cp–P) = 1.0 Hz, Cp); 3.84 (t, *J*(CH_2–P) = 10.0 Hz, $-CH_2-$); −22.6 (t, *J*(P–H) = 12.8 Hz, H); 7.50–8.00 (m, Ph). ^{31}P NMR (H_3PO_4; CD_3COCD_3): δ 54.9 (d, *J*(P–P) = 61.0 Hz); 74.1 (broad).

6b: IR (THF): ν(CO) 2006 (s), 1899 (vs), 1884 (vs), 1854 (vs) cm^{-1}. ^1H NMR (TMS; CD_3COCD_3): δ 4.87 (d, *J*(Cp–P) = 2.0 Hz, Cp); 3.94 (t, *J*(CH_2–P) = 10.0 Hz, $-CH_2-$); −19.0 (t, *J*(P–H) = 9.0 Hz, H); 7.50–8.00 (m, Ph). ^{31}P NMR (H_3PO_4; CD_3COCD_3): δ 29.4 (d, *J*(P–P) = 67.0 Hz); 73.8 (broad).

6c: Anal. Found: C, 34.71; H, 3.81. $C_{19}H_{25}NbO_4P_2$ Calc.: C, 34.78; H, 3.84%. IR (THF): ν(CO) 2002 (s), 1893 (vs), 1874 (vs), 1848 (vs) cm^{-1}. ^1H NMR (TMS; CD_3COCD_3): δ 4.92 (d, *J*(Cp–P) = 2.0 Hz, Cp); 4.15 (t, *J*(CH_2–P) = 10.0 Hz, $-CH_2-$); −19.0 (t, *J*(P–H) = 11.0 Hz, H); 7.50–8.00 (m, Ph). ^{31}P NMR (H_3PO_4; CD_3COCD_3): δ 9.6 (d, *J*(P–P) = 62.0 Hz); 9.6 (dd, *J*(P–P) = 62.0 Hz, *J*(P–^{183}W) = 236.0 Hz); 73.6 (broad).

*3.2.9. Reaction of [Cp_2NbH(dmpm)] and [Cp_2TaH(dmpm)] with [$M'(CO)_4L_2$] (M′ = Cr, Mo or W) (**7a–7c** and **7′a–7′c**)*

The procedure was the same as for **6a–6c**. Complexes **7a–7c** and **7′a–7′c** are deep-green solids. The yields were similar to those observed above.

7a: Anal. Found: C, 44.01; H, 4.86. $C_{19}H_{25}CrNbO_4P_2$ Calc.: C, 43.53; H, 4.81%. IR (THF): ν(CO) 1991 (s), 1889 (vs), 1866 (vs), 1842 (vs) cm^{-1}. ^1H NMR (TMS; CD_3COCD_3): δ 4.93 (d, *J*(Cp–P) = 1.9 Hz, Cp); 1.49 (d, *J*(Me–P) = 6.7 Hz, Me); 1.51 (d, *J*(Me–P) = 5.7 Hz, Me); 2.47 (t, *J*(CH_2–P) = 9.9 Hz, $-CH_2-$); −22.8 (t, *J*(P–H) = 9.3 Hz, H). ^{31}P NMR (H_3PO_4; CD_3COCD_3): δ 24.4 (d, *J*(P–P) = 56.0 Hz); 29.3 (broad).

7b: IR (THF): ν(CO) 1999 (s), 1896 (vs), 1875 (vs), 1846 (vs) cm^{-1}. ^1H NMR (TMS; CD_3COCD_3): δ 4.92 (d, *J*(Cp–P) = 2.0 Hz, Cp); 1.52 (t, *J*(Me–P) = 5.9 Hz, Me); 2.55 (t, *J*(CH_2–P) = 9.8 Hz, $-CH_2-$); −19.0 (broad, H). ^{31}P NMR (H_3PO_4; CD_3COCD_3): δ −4.3 (d, *J*(P–P) = 70.5 Hz); 29.4 (broad).

7c: MS (EI, 70 eV): *m/z* (%) 656 (33.1) $[M]^+$, 432 (100) $[dmpmW(CO)_4]^+$, 404 (58.6), 376 (42.4), 348 (56.1), 244 (88.5) $[Cp_2NbH]^+$. IR (THF): ν(CO) 1995 (s), 1887 (vs), 1864 (vs), 1841 (vs) cm^{-1}. ^1H NMR (TMS; CD_3COCD_3): δ 4.96 (d, *J*(Cp–P) = 1.9 Hz, Cp); 1.53 (d, *J*(Me–P) = 7.2 Hz, Me); 1.66 (d, *J*(Me–P) = 6.2 Hz, Me); 2.81 (t, *J*(CH_2–P) = 9.8 Hz, $-CH_2-$); −19.2 (broad, H). ^{31}P NMR (H_3PO_4; CD_3COCD_3): δ −29.8 (d, *J*(P–P) = 70.0 Hz); −29.8 (dd, *J*(P–P) = 70.0 Hz, *J*(P–^{183}W) = 226.0 Hz); 29.5 (broad).

7′a: IR (THF): ν(CO) 2000 (s), 1907 (vs), 1883 (vs), 1867 (vs) cm^{-1}. ^1H NMR (TMS; C_6D_6): δ 4.32 (s, Cp); 0.76 (d, *J*(Me–P) = 7.0 Hz, Me); 1.16 (d, *J*(Me–P) = 5.9 Hz, Me); 1.61 (t, *J*(CH_2–P) = 9.5 Hz, $-CH_2-$); −23.1 (t, *J*(P–H) = 4.3 Hz, H). ^{31}P NMR (H_3PO_4; C_6D_6): δ 20.2 (d, *J*(P–P) = 63.6 Hz); −19.8 (d, *J*(P–P) = 63.8 Hz).

7′b: IR (THF): ν(CO) 2001 (s), 1896 (vs), 1876 (vs), 1846 (vs) cm^{-1}. ^1H NMR (TMS; C_6D_6): δ 4.30 (d, *J*(Cp–P) = 1.9 Hz, Cp); 0.87 (d, *J*(Me–P) = 7.0 Hz, Me); 1.16 (d, *J*(Me–P) = 5.7 Hz, Me); 1.58 (t, *J*(CH_2–P) = 9.4 Hz, $-CH_2-$); −19.2 (d, *J*(P–H) = 5.9 Hz, H). ^{31}P NMR (H_3PO_4; C_6D_6) δ −9.0 (d, *J*(P–P) = 73.0 Hz); −19.3 (d, *J*(P–P) = 73.0 Hz).

7′c: IR (THF): ν(CO) 1995 (s), 1888 (vs), 1866 (vs), 1841 (vs) cm^{-1}. ^1H NMR (TMS; C_6D_6): δ 4.29 (d, *J*(Cp–P) = 1.7 Hz, Cp); 0.79 (d, *J*(Me–P) = 7.0 Hz, Me); 1.28 (d, *J*(Me–P) = 6.7 Hz, Me); 1.76 (t, *J*(CH_2–P) = 9.3 Hz, $-CH_2-$); −19.3 (d, *J*(P–H) = 4.2 Hz, H). ^{31}P NMR (H_3PO_4; C_6D_6): δ −34.7 (d, *J*(P–P) = 74.0 Hz); −18.1 (d, *J*(P–P) = 74.0 Hz).

3.2.10. Reaction of [Cp_2NbH(dmpe)] with [$M'(CO)_4L_2$] (8a–8c)

These complexes were prepared in a manner analogous to **6a–6c**. This afforded deep green solids of **8a–8c**. The yields were similar to these observed above.

8a: IR (THF): ν(CO) 1989 (s), 1883 (vs), 1865 (vs), 1839 (vs) cm^{-1}. ^1H NMR (TMS; CD_3COCD_3): δ 4.96 (d, *J*(Cp–P) = 1.8 Hz, Cp); 1.42 (d, *J*(Me–P) = 6.9 Hz, Me); 1.52 (d, *J*(Me–P) = 7.9 Hz, Me): 1.70 to 2.09 (m, $-CH_2-$); −21.0 (t, *J*(P–H) = 14.6 Hz, H). ^{31}P NMR (H_3PO_4; CD_3COCD_3): δ 4.1 (s); 56.5 (broad).

8b: IR (THF): ν(CO) 2001 (s), 1894 (vs), 1880 (vs), 1846 (vs) cm^{-1}. ^1H NMR (TMS; CD_3COCD_3): δ 4.96

(d, *J*(Cp–P) = 2.0 Hz, Cp); 1.43 (d, *J*(Me–P) = 6.5 Hz, Me); 1.53 (d, *J*(Me–P) = 7.5 Hz, Me); 1.70–1.98 (m, $-CH_2-$); −18.2 (broad, H). ^{31}P NMR (H_3PO_4; CD_3COCD_3): δ 2.9 (s); 30.1 (broad).

8c: IR (THF): ν(CO) 1996 (s), 1884 (vs), 1866 (vs), 1842 (vs) cm^{-1}. ^{1}H NMR (TMS; CD_3COCD_3): δ 5.01 (d, *J*(Cp–P) = 1.9 Hz, Cp); 1.56 (d, *J*(Me–P) = 6.9 Hz, Me); 1.66 (d, *J*(Me–P) = 7.8 Hz, Me); 1.79–2.20 (m, $-CH_2-$); −18.4 (t, *J*(P–H) = 11.8 Hz, H). ^{31}P NMR (H_3PO_4; CD_3COCD_3): δ −19.1 (s); −19.1 (d, *J*(P–^{183}W) = 216.0 Hz); 11.8 (broad).

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