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Substituted metal carbonyls

XXIII *. Syntheses of unicoordinated diphosphine complexes of Cr and Mo and their entry into heterobimetallics $MM'(CO)_{10}(\mu\text{-P-P})$ $[M, M' = Cr, Mo, W; P\text{-}P = Ph_2P(CH_2)_nPPh_2, n = 2\text{–}4]$ as metalloligands

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Abstract

A series of pentacarbonyl complexes of chromium and molybdenum with unicoordinated-diphosphines, $M(CO)_5(\eta^1\text{-P-P})$ (P-P = dppe, dppp, dppb) has been prepared by amine oxide-induced phosphine substitution of the binary carbonyls. The basicity of the pendant phosphine groups was demonstrated by their ready conversion to the diphosphine-bridged heterobimetallic complexes $(OC)_5M(\mu\text{-P-P})M'(CO)_5$ (M, M' = Cr, Mo, W; M ≠ M') in the presence of $M'(CO)_5(CH_3CN)$. The complexes were characterized by IR and NMR (^1H and $^{31}P\text{-}\{^1H\}$) spectroscopy.

1. Introduction

The most fundamental strategy in heterometallic syntheses is the use of metalloligands as precursors [1]. Since phosphine substitution of metal carbonyl complexes is generally facile, metal complexes bearing pendant phosphine sites seem a natural choice for the synthesis of mixed-metal phosphine carbonyl complexes. It is based on these simple concepts that the unicoordinated diphosphine complexes, *viz.* unidentates, of general formula $M_x(CO)_y(\eta^1\text{-P-P})_z$ (P-P = diphosphine) have been developed. For the Group 6 metals, the most notable examples include $M(CO)_5(dppm)$ (M = Mo, W [2,3]), $M(CO)_5(dppe)$ (M = Cr, W [4,5]), $M(CO)_5(dppp)$ (M = Cr [4]) and $M(CO)_5(dppf)$ (M = Cr, Mo, W; dppf = $Fe(C_5H_4PPh_2)_2$) [6]. Among the several methods developed for their syntheses, direct phosphine substitution on the binary carbonyls seems most general and straightforward [7]. One disadvantage however is its lack of selectivity which makes the pendant phosphine vulnerable to further attack. It is largely because of this that many basic metalloligands carrying a phosphine with a long alkyl chain have not been isolated. In our continuing efforts to activate carbonyl complexes under ambient conditions using amine oxide, we report here the synthesis of the unicoordinated diphosphine complexes of Cr and Mo, $M(CO)_5(\eta^1\text{-P-P})$ (P-P = dppe, dppp, dppb) and their uses as precursors for the synthesis of a complete series of bimetallics $(OC)_5M(\mu\text{-P-P})M'(CO)_5$ (M, M' = Cr, Mo, W; M ≠ M').

2. Results and discussion

When $M(CO)_5(CH_3CN)$ (M = Cr, Mo), prepared *in situ* from $M(CO)_6$ and $(CH_3)_3NO$ in CH_3CN or CH_3CN/thf mixture, is added to a thf solution of the diphosphine (dppe, dppp or dppb), the unidentates are readily formed and can be isolated by preparative tlc. Even though these reactions are stoichiometrically controlled, formation of the thermodynamically stable monobridged dimer, $M_2(CO)_{10}(\mu\text{-P-P})$, as a major by-

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product cannot be avoided. Use of a slight excess of the diphosphine could in most cases (*e.g.* M = Mo, P-P = dppp) improve the yield of the desired unidentates but would also complicate the isolation process which requires the removal of excess phosphines and the dimers.

The IR spectra are typical of that of a pentacarbonyl with a pseudo-C_{4v} structure. The carbonyl absorptions are, as expected, insensitive to the nature of the diphosphines. The discrete methylene resonances in the ^{1}H spectra give the first indication of the non-equivalent phosphine moieties. Metal-coordination of the phosphine imposes a deshielding effect on its neighbouring protons whose shift values are hence comparable to those in the corresponding homometallic dimers. Similarly, shift values of the protons neighbouring the pendant phosphine are similar to those of the free ligands. The ^{31}P-{^{1}H} spectra provide conclusive evidence for the unicoordinated diphosphines. All complexes show a high-field resonance attributed to the pendant phosphine. The similarity in shift of this resonance to that of the free ligand suggests that charge distribution between the two phosphine sites across the alkyl chain is negligible. This agrees with a recent PES study of Mo(CO)$_5$(η^1-P-P) [8]. Among the title complexes, through-chain ^{31}P–^{31}P coupling is observed only when the alkyl chain is short, *viz.* in the dppe complexes.

When the basic metalloligands obtained above are reacted with M′(CO)$_5$(CH$_3$CN), heterometallics of general formula (OC)$_5$M(μ-P-P)M′(CO)$_5$ (M, M′ = Cr, Mo, W; M ≠ M′) are readily formed. In general, either M(CO)$_5$(P-P) or M′(CO)$_5$(P-P) can be used as the precursor; the choice depends on the relative ease of synthesis of the unidentates. Most of the syntheses give a colourless side-product which is strongly retained on the tlc plates. Analysis of a typical mixture from Cr(CO)$_5$(dppe) and W(CO)$_5$(CH$_3$CN) established it to be Cr(CO)$_5$(dppeO), a diphosphine monoxide complex. The analogous W complex has been reported [9]. The phosphoryl functionality is characterized by the ν(P=O) at 1223 and 1214 cm^{-1} in the IR spectrum and low field shift of the oxidized phosphine in the ^{31}P spectrum. The neighbouring presence of an electronegative substituent at the phosphoryl phosphorus raises the ^{31}P–^{31}P coupling from 34 to 46 Hz. This effect of substituent on the coupling magnitude has been previously noted [10]. Similar oxidation of a pendant phosphine by amine oxide has been reported in a dirhenium complex [11]. The observations that the transfer is metal dependent, with the W complex most resistant to oxidation, and the inertness of free diphosphines towards (CH$_3$)$_3$NO suggest that the oxygen transfer is metal-assisted.

All the heterometallic complexes are novel except the dppe-bridged complexes which have been reported by Keiter *et al.* [12]. The additive effect inherent in the two different pentacarbonyl fragments across the diphosphine bridge is a dominant feature in both the IR and NMR spectra. The IR spectrum of the Cr–W dppb complex for example shows two A$_1$ bands at 2072 and 2062 cm^{-1} which belong to the W and Cr fragments respectively. This A$_1$ band generally follows the expected trend of Mo ≥ W > Cr regardless of the nature of the phosphine bridge or the neighbouring metal. Similarly, the ^{1}H spectrum of a heterometallic M–M′ complex is generally a superposition of the spectra of their homometallic M–M and M′–M′ counterparts. The same phenomenon applies to the ^{31}P spectra which give conclusive support to the heterometallics. The ^{31}P–^{31}P couplings found in the dppe-bridged complexes are comparable in magnitude to those in the unidentates. This is in agreement with the non-communicative nature of the two pentacarbonyl moieties. Consequently, the recorded ^{31}P–^{183}W coupling is also insensitive to the neighbouring metal. Also of special interest is the ^{31}P-{^{1}H} spectrum of the Mo–W dppe complex which forms the AB portion of an ABX spectral pattern. The tungsten-bound phosphorus appears as well-defined doublets of triplets due to W–P (239 Hz) and P–P (34 Hz) couplings.

3. Conclusion

In this and previous reports [13], we have shown that singly-bridging diphosphine complexes of both homo- and hetero-metallic complexes can be conveniently prepared through a designed synthesis from the metalloligand. These polymetallic complexes contain different metal moieties which are non-communicative, and which hence maintain their individual chemical characteristics. Current efforts in our laboratory are geared towards the construction of communicative moieties in a polymetallic system. This can be achieved by subsidiary metal–metal interactions either directly or via other auxiliary ligands.

4. Experimental section

4.1. General

All reactions were routinely performed using standard Schlenk techniques under pure dry argon unless otherwise specified. All solvents were freshly distilled over standard drying agents under nitrogen prior to use. All reagents were commercial products and used as supplied. Precoated silica tlc plates of layer thickness 0.25 mm were purchased from Merck or Baker.

IR spectra were recorded in solution cells of pathlength 0.1 mm on a Shimadzu IR-470 or Perkin-Elmer 1600 FT-IR spectrophotometer. The NMR spectra were recorded in $CDCl_3$ solutions on either a JEOL FX 90Q or Bruker AC 300F spectrometer. The ^{31}P spectra were run at 36.23 or 121.49 MHz respectively and externally referenced to 85% H_3PO_4. Elemental analyses were conducted at the Microanalytical Laboratory of our Department. Unless otherwise stated, all ^1H and ^{31}P spectra were recorded in $CDCl_3$ solution. In the ^1H NMR spectral assignments of the unidentate complexes, H_a refers to the methylene protons adjacent to the metal-bound phosphorus and H_b refers to those attached to the uncoordinated phosphorus. H_c corresponds to the inner methylene protons of both dppp and dppb ligands. For the bimetallics, H_a refers to the internal methylene protons of the alkyl chain. H_{Cr}, H_{Mo} and H_W refer to the external protons adjacent to the Cr, Mo and W metal coordination spheres respectively. Experimental yields of the unidentate complexes were computed based on the free ligand consumed while those of the heterometallics were based on the metalloligands.

4.2. Synthesis

4.2.1. $Mo(CO)_5(\eta^1\text{-dppe})$

$Mo(CO)_6$ (0.300 g, 1.14 mmol) was stirred in CH_3CN (20 ml) *in vacuo* with TMNO · $2H_2O$ (0.126 g, 1.13 mmol) for 20 min. The resultant yellow solution was then added dropwise into a continuously stirred solution of dppe (0.453 g, 1.14 mmol) in CH_3CN/thf (2:1) solvent mixture (30 ml) via a teflon transfer tube. The mixture was stirred in argon for 45 min at r.t., after which the volume was reduced by half and stirring continued for another 35 min. The cloudy mixture obtained was allowed to settle to give a white precipitate in a light yellow mother liquor. The white precipitate, identified as $Mo_2(CO)_{10}(\mu\text{-dppe})$ [14] (0.084 g, 10%), was isolated by filtration and recrystallized from CH_2Cl_2/MeOH. The yellow filtrate was evaporated to dryness *in vacuo* and redissolved in a minimum quantity of CH_2Cl_2 and chromatographed on silica tlc plates. Elution with CH_2Cl_2-hexane (1:4), extraction with CH_2Cl_2, followed by further recrystallization from CH_2Cl_2/MeOH led to the isolation of the major product $Mo(CO)_5(\eta^1\text{-dppe})$ (0.153 g, 24%); ν(CO) 2070m, 1982w, 1940vs (cm^{-1}) (CH_2Cl_2); ^1H NMR δ 7.23–7.39 (m, 20H), 2.36 (m, $2H_a$), 1.98 (m, $2H_b$); ^{31}P NMR δ 31.44 (d), ^3J(PP) 36 Hz, −12.09(d), ^3J(PP) 37 Hz; and other side-products, $Mo_2(CO)_{10}(\mu\text{-dppe})$ (0.029 g, 3%) and $Mo(CO)_4(\eta^2\text{-dppe})$ (0.017 g, 3%). ν(CO) (cm^{-1}) 2020m, 1907s, 1881vs (CH_2Cl_2).

4.2.2. $Cr(CO)_5(\eta^1\text{-dppe})$

A similar procedure to that for the Mo analogue was adopted, with the resultant yellow solution being stirred for a longer period of 2.5 h. From the yellow suspension was isolated a white precipitate formulated as $Cr_2(CO)_{10}(\mu\text{-dppe})$ (5%) and a yellow filtrate, which upon separation by preparative tlc, yielded pale yellow crystals of $Cr(CO)_5(\eta^1\text{-dppe})$ (30%); ν(CO) (cm^{-1}) 2063m, 1984w, 1942vs ($CHCl_3$), together with a second crop of $Cr_2(CO)_{10}(\mu\text{-dppe})$ (16%) and $Cr(CO)_4(\eta^2\text{-dppe})$ (5%). ν(CO) (cm^{-1}) 2015m, 1899s, 1881vs (CH_2Cl_2); ^1H NMR δ 7.22–7.42 (m, 20H), 2.45 (m, $2H_a$), 1.98 (m, $2H_b$); ^{31}P NMR δ 50.68(d), ^3J(PP) 34 Hz, −11.64(d), ^3J(PP) 34 Hz. In these preparations of the unidentate complexes, the dimers were always eluted first, followed closely by the unidentates, then the unreacted phosphines, and lastly the more strongly retained chelates.

4.2.3. $Cr(CO)_5(\eta^1\text{-dppp})$

A mixture of $Cr(CO)_6$ (0.400 g, 1.82 mmol) and TMNO · $2H_2O$ (0.202 g, 1.82 mmol) in CH_3CN (30 ml) was stirred *in vacuo* for 20 min, after which it was transferred dropwise to a thf (5 ml) solution of dppp (0.750 g, 1.82 mmol). The resultant yellow solution was then stirred in argon for 1.5 h at r.t., followed by solvent removal to give a pale yellow powdery residue. This residue was extracted with a minimum quantity of CH_2Cl_2 and applied to silica tlc plates. Elution with CH_2Cl_2/MeOH yielded pale yellow $Cr(CO)_5(\eta^1\text{-dppp})$ (0.146 g, 13%), [Found: C, 62.95; H, 4.09; P, 10.00; Cr, 7.88. $C_{32}H_{26}CrO_5P_2$ calc. C, 63.60; H, 4.30; P, 10.25; Cr, 8.60%]. ν(CO) 2065m, 1985w, 1952m, 1941s (cm^{-1}) (Hexane) [4]; ^1H NMR δ 7.35–7.53 (m, 20H), 2.45 (m, $2H_a$), 1.87 (m, $2H_b$), 1.43 (m, $2H_c$); ^{31}P NMR δ 46.58(s), −17.77(s). $Cr_2(CO)_{10}(\mu\text{-dppp})$ [2,15] (0.255 g, 18%) and $Cr(CO)_4(\eta^2\text{-dppp})$ [4,14a] (0.013 g, 1%). ν(CO) (cm^{-1}) 1996m, 1909m, 1877vs (CH_2Cl_2).

4.2.4. $Mo(CO)_5(\eta^1\text{-dppp})$

A similar procedure to the synthesis of the Cr analogue was used except for a different stoichiometric ratio of 1:1:1.2 for $Mo(CO)_6$: TMNO · $2H_2O$: dppp. This ratio afforded a higher yield of the desired unidentate $Mo(CO)_5(\eta^1\text{-dppp})$ (42%) [Found: C, 56.84; H, 3.69; P, 8.76; Mo, 16.20. $C_{32}H_{26}MoO_5P_2$ calc. C, 59.29; H, 4.01; P, 9.55; Mo, 14.80%]; ν(CO) (cm^{-1}) 2072m, 1989w, 1946vs ($CHCl_3$); ^1H NMR δ 7.25–7.45 (m, 20H), 2.48 (dt, $2H_a$) *, $^2J(H_aP)$ 9.2 Hz, $^3J(H_aH_c)$ 6.7 Hz, 2.09 (t, $2H_b$), $^3J(H_bH_c)$ 7.5 Hz, 1.47 (m, $2H_c$); ^{31}P NMR δ 27.13(s), −18.11(s); and reduced the formation of the dimer $Mo_2(CO)_{10}(\mu\text{-dppp})$ [15] (9%).

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* doublets of triplets (dt) splitting pattern not well resolved as $^2J(HP) \approx {}^3J(HH)$.

However, purification of the product was hampered by the contaminating $Mo_2(CO)_{10}(\mu\text{-dppp})$ which could not be completely removed despite repeated recrystallizations or tlc elutions.

4.2.5. $Cr(CO)_5(\eta^1\text{-dppb})$

A mixture of $Cr(CO)_6$ (0.300 g, 1.36 mmol) and $TMNO \cdot 2H_2O$ (0.152 g, 1.37 mmol) in CH_3CN (30 ml) was stirred *in vacuo* for 20 min. The volume of this yellow solution was reduced by half before it was slowly transferred into a continuously stirred solution of dppb (0.582 g, 1.37 mmol) in thf (30 ml). This resultant mixture was then stirred under argon for 20 h at r.t. and the unreacted dppb was precipitated by solution concentration *in vacuo*. The filtrate was evaporated to dryness and redissolved in a minimum quantity of CH_2Cl_2 and chromatographed on silica tlc plates. Elution with CH_2Cl_2-hexane (1 : 3) yielded three major products, with the following elution order, *viz*. white powder of $Cr_2(CO)_{10}(\mu\text{-dppb})$ [15] (0.162 g, 20%), yellow oil of $Cr(CO)_5(\eta^1\text{-dppb})$ (0.100 g, 16%). ν(CO) (cm^{-1}) 2062m, 1983w, 1939vs ($CHCl_3$); ^1H NMR δ 7.29–7.48 (m, 20H), 2.32 (dt, $2H_a$) *, $^2J(H_aP)$ 8.2 Hz; $^3J(H_aH_c)$ 6.9 Hz, 1.97 (m, $2H_b$), 1.46 (m, $4H_c$); ^{31}P NMR δ 45.97(s), −16.09(s) and, yellow powder of $Cr(CO)_4(\eta^2\text{-dppb})$ [16] (0.153 g, 26%). ν(CO) (cm^{-1}) 1998m, 1905m, 1880vs (CH_2Cl_2). All the products were further purified by recrystallization from CH_2Cl_2/MeOH.

4.2.6. $Mo(CO)_5(\eta^1\text{-dppb})$

The procedure is similar to that of the synthesis of the Cr complex but with a reaction time of 19 h. Off-white crystals of $Mo(CO)_5(\eta^1\text{-dppb})$ (16%) [Found: C, 59.51; H, 4.05; P, 9.69; Mo, 14.57. $C_{34}H_{28}MoO_5P_2$ calc: C, 59.83; H, 4.23; P, 9.36; Mo, 14.50%]; ν(CO) (cm^{-1}) 2072m, 1988w, 1945vs ($CHCl_3$); ^1H NMR δ 7.29–7.48 (m, 20H), 2.32 (dt, $2H_a$) *, $^2J(H_aP)$ 8.5 Hz, $^3J(H_aH_c)$ 6.9 Hz, 1.97 (m, $2H_b$), 1.46 (m, $4H_c$); ^{31}P NMR δ 27.40(s), −16.11(s); were isolated, together with $Mo(CO)_4(\eta^2\text{-dppb})$ [17] (10%). ν(CO) (cm^{-1}) 2025m, 1920s, 1990vs (CH_2Cl_2).

For comparison, the spectra of the free ligands were also recorded. Dppe: ^1H NMR δ 7.28–7.39 (m, 20H), 2.09 (m, $4H_b$); ^{31}P NMR δ −11.98(s); dppp: ^1H NMR δ 7.24–7.45 (m, 20H), 2.20 (m, $4H_b$), 1.60 (m, $2H_c$); ^{31}P NMR δ −16.83(s); dppb: ^1H NMR δ 7.25–7.45 (m, 20H), 2.02 (m, $4H_b$), 1.63 (m, $4H_c$); ^{31}P NMR δ −15.48(s).

4.2.7. $(OC)_5M(\mu\text{-dppe})M'(CO)_5$ (M, M′ = Cr, Mo, W; M ≠ M′)

4.2.7.1. M = Mo, M′ = Cr.

$Cr(CO)_6$ (0.052 g, 0.24 mmol) was stirred in thf (20 ml) *in vacuo* with $TMNO \cdot 2H_2O$ (0.026 g, 0.23 mmol) for 20 min. This yellow mixture was then filtered into a flask containing a thf solution (10 ml) of $Mo(CO)_5(\eta^1\text{-dppe})$ (0.100 g, 0.16 mmol), via a teflon transfer tube and stirred under argon for 20 h at r.t. After the removal of solvent *in vacuo*, the residue was extracted with a minimum amount of CH_2Cl_2 and applied to silica tlc plates. Elution with CH_2Cl_2-hexane (1 : 3) followed by further recrystallization from CH_2Cl_2/MeOH gave rise to $(OC)_5Mo(\mu\text{-dppe})Cr(CO)_5$ (0.010 g, 11%) [Found: C, 52.09; H, 2.82. $C_{36}H_{24}CrMoO_{10}P_2$ calc: C, 52.32; H, 2.90%]. ν(CO) (cm^{-1}) 2073m, 2063m, 1987w, 1948vs ($CHCl_3$); ^1H NMR δ 7.22–7.48 (m, 20H), 2.20 (s, 4H); ^{31}P NMR δ 51.56(d), $^3J(PP)$ 30 Hz, 32.24(d); $^3J(PP)$ 34 Hz; and a side-product tentatively assigned as *trans*-$Cr(CO)_4[(dppe)Mo(CO)_5]_2$, (0.012 g, 8%) [Found: C, 55.19; H, 3.38; P, 9.02; Cr, 3.25; Mo, 13.44. $C_{66}H_{48}CrMo_2O_{14}P_4$ calc: C, 55.32; H, 3.35; P, 8.65; Cr, 3.63; Mo, 13.39%].

4.2.7.2. M = Cr, M′ = W.

The Cr–W product (0.028 g, 20%) [Found: C, 50.28; H, 2.75. $C_{36}H_{24}CrO_{10}P_2W$ calc: C, 47.29; H, 2.62%] was prepared similarly from $Cr(CO)_5(\eta^1\text{-dppe})$ (0.100 g, 0.17 mmol), $TMNO \cdot 2H_2O$ (0.028 g, 0.25 mmol) and $W(CO)_6$ (0.089 g, 0.25 mmol) with a reaction time of 23 h. ν(CO) (cm^{-1}) 2072w, 2063m, 1984w, 1944vs ($CHCl_3$); ^1H NMR δ 7.22–7.48 (m, 20H), 2.25 (s, 4H); ^{31}P NMR δ 51.29(d), $^3J(PP)$ 30 Hz, 13.53(d), $^3J(PP)$ 34 Hz. A side-product extracted from the baseline of the tlc plates was analysed as $Cr(CO)_5(Ph_2PCH_2CH_2P(O)Ph_2)$ (0.016 g, 17%) [Found: C, 60.29; H, 4.02. $C_{31}H_{24}CrO_6P_2$ calc: C, 61.39; H, 3.96%]. ν(CO) (cm^{-1}) 2064m, 1985w, 1939vs and ν(PO) 1223m, 1214vs ($CHCl_3$).

4.2.7.3. M = Mo, M′ = W.

White crystals of $(OC)_5Mo(\mu\text{-dppe})W(CO)_5$ (0.013 g, 15.6%) [Found: C, 45.42; H, 2.50. $C_{36}H_{24}MoO_{10}P_2W$ calc: C, 45.12; H, 2.50%] were similarly obtained from $Mo(CO)_5(\eta^1\text{-dppe})$ (0.055 g, 0.09 mmol), $TMNO \cdot 2H_2O$ (0.015 g, 0.14 mmol) and $W(CO)_6$ (0.046 g, 0.13 mmol) with a reaction time of 17 h. ν(CO) (cm^{-1}) 2072m, 1985w, 1947vs ($CHCl_3$); ^1H NMR δ 7.22–7.54 (m, 20H), 2.26 (s, 4H); ^{31}P NMR δ 32.10(d), $^3J(PP)$ 34 Hz, 13.39(dt); $^3J(PP)$ 34 Hz, $J(WP)$ 239 Hz.

All the percentage yields were calculated based on the amount of unidentate, $Mo(CO)_5(\eta^1\text{-dppe})$, consumed.

4.2.8. $(OC)_5M(\mu\text{-dppp})M'(CO)_5$ (M, M′ = Cr, Mo, W; M ≠ M′)

The title complexes were prepared as described in the form of their dppe analogues with a stoichiometric ratio of 1.0 : 1.5 : 1.5 [$M(CO)_5(\eta^1\text{-dppp})$: $M'(CO)_6$:

TMNO · $2H_2O$]. $Cr(CO)_5(\eta^1$-dppp) was used as the precursor for the Cr-W complex whilst $Mo(CO)_5(\eta^1$-dppp) was used for the Cr-Mo and Mo-W complexes. M = Cr, M′ = W (Yield: 40%). M = Mo, M′ = Cr (Yield: 5%) [Found: C, 51.96; H, 2.56. $C_{37}H_{26}$-$CrMoO_{10}P_2$ calc: C, 52.89; H, 3.09%]. ν(CO) (cm^{-1}) 2063w, 2072m, 1987w, 1945vs ($CHCl_3$); ^1H NMR δ 7.35–7.43 (m, 20H), 2.39 (m, $4H_{Cr,Mo}$), 1.27 (m, $2H_a$); ^{31}P NMR δ 46.01(s), 27.02(s). M = Mo, M′ = W (Yield: 32%) [Found: C, 46.92; H, 2.54; P, 7.17; Mo, 11.64; W, 19.18. $C_{37}H_{26}MoO_{10}P_2W$ calc: C, 45.71; H, 2.67; P, 6.37; Mo, 9.87; W, 18.91%]. ν(CO) (cm^{-1}) 2072m, 1983w, 1943vs ($CHCl_3$); ^1H NMR δ 7.33–7.42 (m, 20H), 2.50 (dt, $2H_W$), $^2J(H_WP)$ 9.2 Hz, $^3J(H_WH_a)$ 7.2 Hz, 2.40 (dt, $2H_{Mo}$), $^2J(H_{Mo}P)$ 9.8 Hz, $^3J(H_WH_{Mo})$ 6.5 Hz, 1.27 (m, $2H_a$); ^{31}P NMR δ 27.06(s), 8.66(t), J(WP) 238 Hz. The Cr-W complex isolated [ν(CO) (cm^{-1}) 2062m, 1983w, 1939vs ($CHCl_3$); ^1H NMR δ 7.35–7.43 (m, 20H), 2.39 (dt, $4H_{Cr,W}$), $^2J(H_{Cr,W}P)$ 9.4 Hz, $^3J(H_{Cr,W}H_a)$ 6.9 Hz, 1.23 (m, $2H_a$); ^{31}P NMR δ 46.03(s), 8.63(t), J(WP) 238 Hz] was heavily contaminated with $Cr_2(CO)_{10}(\mu$-dppp). Removal of this contaminant could not be achieved by recrystallizations or tlc elutions. A yellow side-product tentatively analysed as $Cr(CO)_4[(dppp)Mo(CO)_5]_2$, (7 mg, 4%) [Found: C, 55.86; H, 3.61. $C_{70}H_{52}CrMo_2O_{14}P_2$ calc: C, 55.92; H, 3.56%] was isolated in the reaction of $Mo(CO)_5(\eta^1$-dppp) with $Cr(CO)_6$ and TMNO · $2H_2O$.

4.2.9. *$(OC)_5M(\mu$-dppb)$M'(CO)_5$ (M, M′ = Cr, Mo, W; M ≠ M′)*

The Mo-W complex was prepared from $Mo(CO)_5$ (η^1-dppb) and those of Cr-Mo and Cr-W from the Cr metalloligand. A typical procedure is represented in the preparation of the Cr-Mo complex which involved the filtration of a yellow mixture of $Mo(CO)_6$ (0.064 g, 0.24 mmol) and TMNO (0.027 g, 0.24 mmol) into a solution of $Cr(CO)_5(\eta^1$-dppb) (0.100 g, 0.16 mmol) in CH_3CN (30 ml) and the resultant mixture was stirred for 20 h at r.t. Separation by preparative tlc (eluted with 25% CH_2Cl_2 in hexane), followed by recrystallization with CH_2Cl_2/MeOH led to the isolation of analytically pure white crystalline complexes of the heterometallics. M = Cr, M′ = Mo (0.093 g, 67%) [Found: C, 53.68; H, 3.12; P, 7.42; Cr, 6.39; Mo, 10.53. $C_{38}H_{28}CrMoO_{10}P_2$ calc: C, 53.43; H, 3.28; P, 7.25; Cr, 6.08; Mo, 11.23%] ν(CO) 2072m, 2062m, 1984w, 1942vs (cm^{-1}) ($CHCl_3$); ^1H NMR δ 7.40–7.46 (m, 20H), 2.30 (m, $4H_{Cr,Mo}$), 1.36 (m, $4H_a$); ^{31}P NMR δ 45.90(s), 27.35(s). M = Cr, M′ = W (Yield: 58%) [Found: C, 48.72; H, 2.67; P, 6.85; Cr, 5.33; W, 19.61. $C_{38}H_{28}CrO_{10}P_2W$ calc: C, 48.44; H, 2.97; P, 6.57; Cr, 5.52; W, 19.5%]. ν(CO) 2070m, 2062m, 1982w, 1939vs (cm^{-1}) ($CHCl_3$); ^1H NMR δ 7.41–7.47 (m, 20H), 2.42 (dt, $2H_W$) [**], $^2J(H_WP)$ 7.2 Hz, $^3J(H_WH_a)$ 8.9 Hz, 2.34 (dt, $2H_{Cr}$) [**], $^2J(H_{Cr}P)$ 7.3 Hz, $^3J(H_aH_{Cr})$ 8.3 Hz, 1.38 (m, $4H_a$); ^{31}P NMR δ 45.95(s), 9.15(t), J(WP) 239 Hz. M = Mo, M′ = W (Yield: 24%) [Found: C, 46.40; H, 2.78; P, 6.77; Mo, 9.31; W, 22.66. $C_{38}H_{28}MoO_{10}P_2W$ calc: C, 46.28; H, 2.84; P, 6.28; Mo, 9.73; W, 18.64%]. ν(CO) (cm^{-1}) 2071m, 1983w, 1941vs ($CHCl_3$); ^1H NMR δ 7.40–7.45 (m, 20H), 2.42 (dt, $2H_W$) [**], $^2J(H_WP)$ 7.4 Hz, $^3J(H_aH_W)$ 7.6 Hz, 2.30 (dt, $2H_{Mo}$) [**], $^2J(H_{Mo}P)$ 7.3 Hz, $^3J(H_aH_{Mo})$ 7.6 Hz, 1.39 (m, $4H_a$); ^{31}P NMR δ 27.36(s), 9.12(t), J(WP) 239 Hz.

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