Substituted Metal Carbonyls. Part 24.[1] Heteropolymetallic Oligomers $[(OC)_xM'(\mu\text{-L–L})M(CO)_4(\mu\text{-L–L})M'(CO)_x]$ and $[(OC)_5Mn\text{–}Mn(CO)_4(\mu\text{-L–L})M(CO)_4(\mu\text{-L–L})(OC)_4Mn\text{–}Mn(CO)_5]$ [M = Cr, Mo or W; M' = Cr, Mo, W ($x = 5$) or Fe ($x = 4$); L–L = $Fe(C_5H_4PPh_2)_2$ or $Ph_2P(CH_2)_mPPh_2$ (m = 2 or 3)], with Metal Carbonyl and Diphosphine Repeating Units

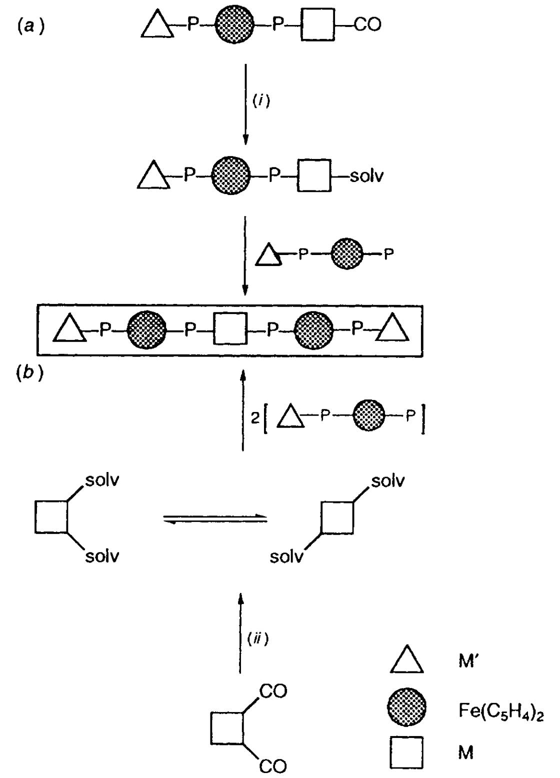
Lai-Tee Phang, Kim-Suan Gan, Hian Kee Lee and T. S. Andy Hor*
Department of Chemistry, Faculty of Science, National University of Singapore, Kent Ridge 0511, Singapore

A series of soluble oligomeric complexes of formulae $[(OC)_xM'(\mu\text{-L–L})M(CO)_4(\mu\text{-L–L})M'(CO)_x]$ [L–L = $Fe(C_5H_4PPh_2)_2$: M = Cr, M' = Cr, Mo, W, Fe, or Mn_2; M = Mo, M' = Cr, Mo, Fe or Mn_2; M = W, M' = Cr or W. L–L = $Ph_2P(CH_2)_mPPh_2$: M = Cr, M' = Mo, m = 2 or 3. M' = Cr, Mo, or W, x = 5; M' = Fe, x = 4; M' = Mn_2, x = 9) has been isolated either as by-products in the syntheses of the bimetallics $[(OC)_xM'(\mu\text{-L–L})M(CO)_x]$ or in a designed synthesis from *cis*-$[M(CO)_4(solv)_2]$ (solv = solvent) (yields 1–18%). The repeating units are ferrocenyl or alkyl-chain diphosphine and metal carbonyl fragments and sometimes the oligomeric chains are supported by a M–M bond. The longest polymeric chain consists of seven metal atoms, Fe_2MMn_4. The linearity of the oligomeric propagation depends on the geometry of the central $M(CO)_4$ unit, which is *cis* for Mo but *trans* for Cr or W. The geometrical preference is explained on steric and thermodynamic grounds, and the fluxionality of the five-co-ordinate intermediate. Nucleophilic attack by Me_3NO on the bimetallics did not give oligomers through decarbonylation, but rather the phosphine oxide complexes $[M(CO)_5\{Fe(C_5H_4PPh_2)(C_5H_4PPh_2O)\}]$ through dephosphination.

One of the major advances in recent years in organometallic chemistry is the synthesis of organometallic oligomers and polymers.[2] It is an intuitively simple idea to construct a polymer chain based on metal co-ordination spheres and organic substrates as bridging units. In practice, however, it remains a formidable challenge to design soluble polymers from basic monomeric units under controlled conditions. So far success has been met in some of these designs which are largely centred on the π-conjugated systems.[3] Our recent work[1,4] in the synthesis of heterobimetallics from mononuclear complexes with pendant phosphines has prompted us to extend this methodology to oligomeric designs. One obvious approach is to activate a bimetallic substrate through carbonyl substitution. Subsequent attachment of an incoming metalloligand would hence give rise to a longer polymeric chain [Scheme 1(*a*)]. An alternative strategy is a designed synthesis using an unsaturated substrate with two vacant sites. This would allow for one-dimensional propagation especially when the two sites are *trans*-disposed [Scheme 1(*b*)]. In this paper we examine these approaches and report the novel oligomeric complexes thus synthesised.

Results and Discussion

Attempts were first made to decarbonylate a series of bimetallics,* $[(OC)_xM(\mu\text{-dppf})M'(CO)_x]$ [M, M' = Cr, Mo, W ($x = 5$) or Fe ($x = 4$), M ≠ M'; dppf = 1,1'-bis(diphenylphosphino)ferrocene)] and homometallics (M = M') under



Scheme 1 Representation of the preparation of the oligomeric polyheterometallics from the heterodimetallics (*a*) and the mononuclear unsaturated substrates (*b*). (*i*) Me_3NO, solvent (solv); (*ii*) solv, heat or Me_3NO

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* A complex of formula $(OC)_xM(\mu\text{-dppf})M'(CO)_x$ is regarded as bimetallic in the sense that there are two carbonyl-bearing metals. However since the bridging dppf is ferrocenyl based, the complex is strictly trimetallic.

various conditions (thermolytic, UV-photolytic, or Me_3NO-induced) either in the presence or absence of added phosphines. Generally, the reactions either do not occur or proceed sluggishly. Under more forceful conditions (for example, photolysis over 5 h, refluxing in toluene, or an excess of amine oxide) the complexes break down to the corresponding chelates, $[M(CO)_4(dppf\text{-}P,P')]$ (M = Cr, Mo or W) or $[Fe(CO)_3(dppf\text{-}P,P')]$. This contrasts with the monophosphine complex $[M(CO)_5(PR_3)]$ or $[Fe(CO)_4(PR_3)]$ which readily undergoes carbonyl substitution to give the disubstituted analogues.[5] In the amine oxide reactions significant quantities of the phosphine oxide complexes $[M(CO)_5(dppfo\text{-}P)]$ or $[Fe(CO)_4(dppfo\text{-}P)]$ are formed in which the dppf ligand is unidentate and its dangling phosphorus atom oxidised to a phosphoryl group.[6] These phosphine oxide complexes are readily characterised by NMR $[\delta(^{31}P) \approx 29]$ and IR $[\nu(P{=}O) \approx 1120\ cm^{-1}]$[6] spectroscopy. Preferential transfer of oxygen from Me_3NO to the co-ordinated phosphine instead of the carbonyl sites poses a significant problem in these oligomeric syntheses; a similar phenomenon has been reported in a related rhenium system.[6] This further illustrates that co-ordinated phosphine is also susceptible to nucleophilic attack by amine oxide. Oxidative decarbonylation by amine oxide has been discussed in depth recently by Basolo and co-workers.[7]

In view of the inertness of the dppf-bridged complexes towards carbonyl replacement, we turned our attention to the other route, *i.e.* the use of *cis*-$[M(CO)_4(solv)_2]$ (solv = labile solvent) as substrates [Scheme 1(*b*)]. A typical reaction between *cis*-$[Mo(CO)_4(MeCN)_2]$ and $[Cr(CO)_5(dppf\text{-}P)]$ (1:2) gives $[(OC)_xM'(\mu\text{-}dppf)M(CO)_4(\mu\text{-}dppf)M'(CO)_x]$ (M = Mo, M′ = Cr, *x* = 5). The congeneric M = W, M′ = Cr complex was similarly synthesised. Other complexes with M = Cr, M′ = Mo, W or Fe and M = Mo, M′ = Fe were isolated as by-products in trace to minor quantities in the syntheses of the heterobimetallics $[(OC)_xM(\mu\text{-}dppf)M'(CO)_x]$ from $[M(CO)_x(solv)_2]$ and $[M'(CO)_x(dppf\text{-}P)]$. To show that the ferrocenyl moieties of the dppf ligand play no significant role in the oligomeric assembly, we also isolated as side-products the analogous M = Cr, M′ = Mo complexes using the alkyl-chain diphosphines dppe and dppp as the bridging units in the bimetallic synthesis of $[(OC)_5Cr\{\mu\text{-}Ph_2P(CH_2)_mPPh_2\}Mo(CO)_5]$ [*m* = 2 (dppe) or 3 (dppp)]. This type of molecular assembly can also be extended to longer oligomeric chains when the substrate is a dinuclear complex with a pendant phosphine. This is illustrated in the synthesis of $[(OC)_5Mn\text{-}Mn(CO)_4(\mu\text{-}dppf)Mo(CO)_4(\mu\text{-}dppf)(OC)_4Mn\text{-}Mn(CO)_5]$ from *cis*-$[Mo(CO)_4(MeCN)_2]$ and $[Mn_2(CO)_9(dppf\text{-}P)]$[6] (1:2). The chromium analogue was isolated as a by-product in the synthesis of $[(OC)_5Mn\text{-}Mn(CO)_4(\mu\text{-}dppf)Cr(CO)_5]$.[4c] The same strategy could also be applied to the syntheses of the homometallic oligomers when M = M′ = Cr, Mo or W with dppf functioning as the bridging unit. A list of these complexes and their pertinent synthetic and spectroscopic data is given in Table 1.

All the complexes are characterised by IR and NMR (^1H and $^{31}P\text{-}\{^1H\}$) spectroscopies. The M = Cr, M′ = Mo complex was also studied by $^{13}C\text{-}\{^1H\}$ NMR spectroscopy. The additive effects observed in the heterobimetallic complexes are also present in these spectra. This is a good indication that the repeating units on the polymer chain retain much of their integrity thus implying a lack of electron delocalisation along the chain. The carbonyl region in the IR spectra consists of bands which are characteristic of penta- and tetra-carbonyl moieties. All the M = Cr or W complexes are *trans*-oriented with respect to the central $M(CO)_4$ moiety whilst the molybdenum analogues are exclusively *cis*, regardless of the nature of the bridging phosphine. This can be inferred by comparing the tetracarbonyl portion of the spectrum with the spectra of *cis*- and *trans*-$[M(CO)_4(PPh_3)_2]$. In the ^1H NMR spectra the cyclopentadienyl protons of the dppf complexes generally give four discrete resonances due to the inequivalence of the two ferrocenyl phosphine groups when binding to different metals. Homonuclear ($^1H\text{-}^1H$) decoupling experiments were needed to identify the matching resonances belonging to the same C_5H_4 ring. The ^{31}P chemical shift values are similar to those found for the mono- and bi-metallic complexes. The geometry of the central $M(CO)_4$ unit is reflected in its phosphorus co-ordination shift (Δ). For example, Δ for the M = Cr, M′ = Mo complex (82.0 ppm) is similar to that of *trans*-$[Cr(CO)_4(PPh_3)_2]$ (77.8 ppm).[8] On the other hand, Δ for the M = Mo, M′ = Mo complex (44.0 ppm) is nearly identical to that of *cis*-$[Mo(CO)_4(PPh_3)_2]$ (43.0 ppm).[9] No $^{31}P\text{-}^{31}P$ coupling is observed for all the listed complexes except the dppe complex of M = Cr, M′ = Mo in which the alkyl chain is relatively short. The ^{31}P NMR spectrum shows a second-order AA′XX′ pattern which is centrosymmetric, as with all spectra of a $AA'X_nX_n'$-type spin system.[10] Half of the total intensity of the spectrum is contributed by two sets of doublets, each of which represents the a (P_{Cr}) and x (P_{Mo}) sub-spectra. The doublet separation corresponds to the sum of $^3J(PP)$ and $^5J(PP)$ (30 Hz). The remaining intensity is divided between one pair of inner and one pair of outer lines in each a or x sub-spectrum. The through-metal $^2J(PP)$ can be directly measured from the separation between the outer and the first inner lines. This spectrum lends strong support to the oligomeric structure. The carbonyl resonances in the ^{13}C NMR spectra also confirm the presence of individual carbonyl fragments. The spectrum of the M = Cr, M′ = Mo dppf complex understandably gives a single triplet resonance for the equivalent carbonyls on a *trans*-$[Cr(CO)_4P_2]$ sphere [δ 223.1, $^2J(PC)$ 12.8 Hz]. This is in contrast with the two resonances found for *cis*-$[Cr(CO)_4(dppf\text{-}P,P')]$ [δ 226.0, *J*(PC) 8.5; 222.2, *J*(PC) 14.1 Hz].[11]

These species represent a new class of soluble organometallic oligomers which are assembled by linking up the carbonyl fragments to diphosphines. These are illustrated in Scheme 2 using dppf ligand as an example. They can be classified into three types: (*a*) a trimetallic oligomer with a Group 6 tetracarbonyl moiety sandwiched between two octahedral spheres (**I**); (*b*) as (*a*) but the peripheral spheres are trigonal bipyramidal iron(0) carbonyls (**II**); (*c*) a pentametallic oligomer made up of two units of dimanganese carbonyls and a Group 6 tetracarbonyl (**III**). Types **I** and **II** are 'non-communicative' oligomers as the bonding between (and within) the repeating units is predominantly σ in character. Type **III** can be considered 'semi-communicative' as the repeating units are linked both by diphosphines and direct Mn–Mn bonds. Within these three types there are are two variations. First, the presence of a ferrocenyl diphosphine would in principle increase the metal content of the oligomer; the $[MMn_4]$ complex may now be considered as a heptametallic $[Fe_2MMn_4]$ oligomer with $C_5H_4PPh_2$ serving as a bridging link. Secondly, the oligomer can be propagated linearly or angularly depending on the local geometry of the metal sphere at the centre of the chain. The *trans* orientation as found in the complexes of Cr and W would promote the unidirectionality of the oligomers.

Among the Group 6 metals, the M = Cr oligomers are formed most readily as by-products in the bimetallic syntheses, *viz.* $[M(CO)_6] + Me_3NO + [M'(CO)_x(dppf\text{-}P)]$. The analogous complexes of Mo and W are best made by design from *cis*-$[M(CO)_4(solv)_2]$ as they are only formed in trace quantities in the bimetallic syntheses. Since we have ruled out their formation by carbonyl displacement from the bimetallics, the active precursors are likely to be the unsaturated $[M(CO)_4L(solv)]$ [L = $M'(CO)_5(L\text{-}L\text{-}P)$, $Fe(CO)_4(L\text{-}L\text{-}P)$, or $Mn_2(CO)_9(L\text{-}L\text{-}P)$] which is formed directly by solvent displacement from $[M(CO)_4(solv)_2]$ by L. Although generation of the oligomers in the designed synthesis is easily understood, their more facile formation in the M = Cr reaction mixture in the bimetallic syntheses in comparison to the mixtures with M = Mo or W seems unusual as Basolo and co-workers[12] have demonstrated that the rate of Me_3NO-induced carbonyl displacement on both $[M(CO)_6]$ and

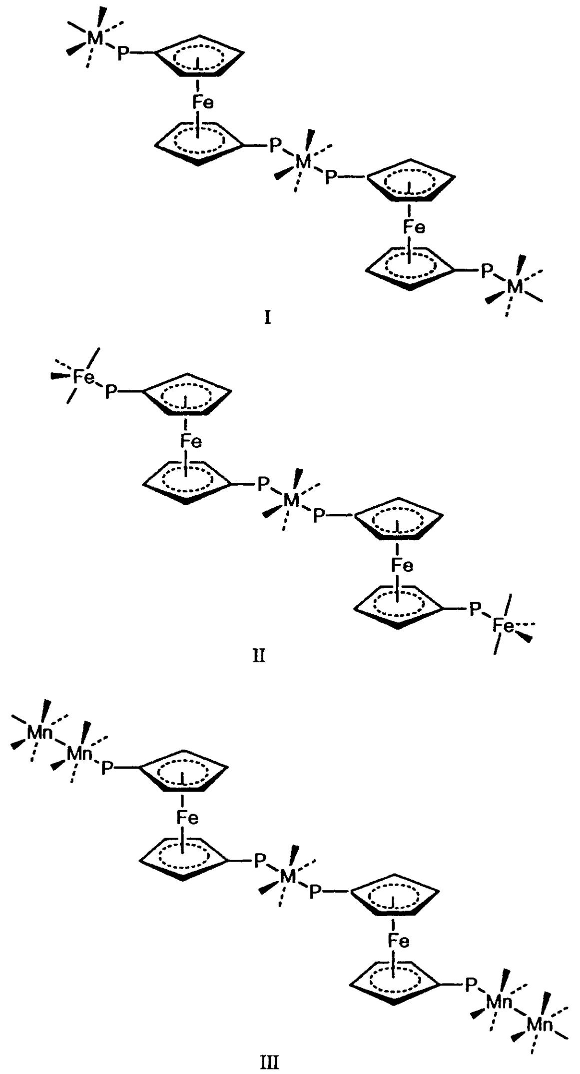
Table 1 Synthetic and spectroscopic data for $[(OC)_xM'(\mu\text{-L-L})M(CO)_4(\mu\text{-L-L})M'(CO)_x]$ [L–L = $Fe(C_5H_4PPh_2)_2$: M = Cr, M′ = Cr, Mo, W, Fe or Mn_2; M = Mo, M′ = Cr, Mo, Fe or Mn_2; M = W, M′ = Cr or W. L–L = $Ph_2P(CH_2)_mPPh_2$: M = Cr, M′ = Mo, *m* = 2 or 3. M′ = Cr, Mo or W, *x* = 5; M′ = Fe, *x* = 4; M′ = Mn_2, *x* = 9]

Complex (diphosphine ligand)	Substrates, solvent, yield	$\tilde{\nu}(CO)/cm^{-1}$	$\delta(^1H)$[a]	$\delta(^{31}P)$, *J*/Hz
Cr–Cr–Cr (dppf)	$[Cr(CO)_6]$ + Me_3NO + dppf (1.0:0.8:0.4), thf + CH_2Cl_2, 4%	2063m, 2007vw, 1990w, 1940vs, 1886s	7.41–7.34 (m, 40 H), 4.20 (m, 4 H^{Cr}), 4.11 (m, 4 H^{Cr} + 4 $H_b^{Cr'}$), 3.95 (q, 4 $H_a^{Cr'}$)[b,c]	64.8 (s, Ph_2PCr), 46.8 (s, Ph_2PCr')[b]
Mo–Cr–Mo (dppf)	$[Cr(CO)_6]$ + Me_3NO + $[Mo(CO)_5(dppf\text{-}P)]$ (1.4:1.3:1.0), thf, 15%	2072m, 1991w, 1946vs, 1886s	7.40–7.29 (m, 40 H), 4.23 (m, 4 H^{Cr}), 4.12 (m, 4 H^{Cr}), 4.10 (m, 4 H_b^{Mo}), 3.95 (q, 4 H_a^{Mo})[b,c]	64.8 (s, Ph_2PCr), 27.9 (s, Ph_2PMo)[b]
W–Cr–W (dppf)	$[Cr(CO)_6]$ + Me_3NO + $[W(CO)_5(dppf\text{-}P)]$ (1.4:1.3:1.0), thf, 4%	2071m, ≈2000vw, 1981w, 1938vs, 1886s	7.40–7.29 (m, 40 H), 4.23 (m, 4 H^{Cr}), 4.12 (m, 4 H^{Cr} + 4 H_b^{W}), 3.94 (q, 4 H_a^{W})[b,c]	64.8 (s, Ph_2PCr), 10.9 [t, Ph_2PW, *J*(PW) 247[b,d]]
Fe–Cr–Fe (dppf)	$[Cr(CO)_6]$ + Me_3NO + $[Fe(CO)_4(dppf\text{-}P)]$ (1.4:1.3:1.0), thf, 3%	*e*	7.42–7.38 (m, 40 H), 4.21 (m, 4 H), 4.17 (m, 4 H), 4.01 (m, 4 H), 3.82 (q, 4 H)[f]	67.0 (s, Ph_2PFe), 65.2 (s, Ph_2PCr)[f]
Mn_2–Cr–Mn_2 (dppf)	$[Cr(CO)_6]$ + Me_3NO + $[Mn_2(CO)_9(dppf\text{-}P)]$ (1.4:1.3:1.0), thf, 3%	2091w, ≈2000vw, 1982s, 1920m, 1893m	*g*	65.6 (br s, Ph_2PMn), 64.6 (s, Ph_2PCr)[b]
Mo–Mo–Mo (dppf)	$[Mo(CO)_6]$ + Me_3NO + dppf (1.0:0.8:0.4), thf + CH_2Cl_2, 2%	2072m, 2020w, 1991w, 1947s, 1900(sh)	7.36–7.23 (m, 30 H), 7.10–6.98 (m, 10 H), 4.34 (m, 4 $H_b^{Mo'}$), 4.15 (m, 4 H^{Mo}), 3.99 (q, 4 $H_a^{Mo'}$), 3.72 (m, 4 H^{Mo})[b,c]	27.9 (s, Ph_2PMo'), 26.8 (s, Ph_2PMo)[b,d]
Cr–Mo–Cr (dppf)	$[Mo(CO)_6]$ + Me_3NO in MeCN + $[Cr(CO)_5(dppf\text{-}P)]$ (1:2:2), thf + MeCN, 18%	2062m, 2019w, 1981w, 1938s, 1901(sh)	7.38–7.23 (m, 30 H), 7.10–6.96 (m, 10 H), 4.33 (m, 4 H_b^{Cr}), 4.11 (m, 4 H^{Mo}), 4.00 (q, 4 H_a^{Cr}), 3.72 (m, 4 H^{Mo})[b,c]	46.9 (s, Ph_2PCr) 26.8 (s, Ph_2PMo)[b,d]
Fe–Mo–Fe (dppf)	(*a*) $[Mo(CO)_6]$ + Me_3NO + $[Fe(CO)_4(dppf\text{-}P)]$ (1.4:1.3:1.0), thf, 6%; (*b*) $[Mo(CO)_6]$ + Me_3NO in MeCN + $[Fe(CO)_4(dppf\text{-}P)]$ (1.0:2.5:2.0), thf + MeCN, 9%	2050m, 2020w, 1975w, 1931s, 1900(sh)	7.43–7.27 (m, 30 H), 7.13–7.00 (m, 10 H), 4.38 (m, 4 H), 4.26 (m, 4 H), 3.76 (m, 4 H), 3.66 (m, 4 H)[b,h]	66.4 (s, Ph_2PFe), 26.7 (s, Ph_2PMo)[b,d]
Mn_2–Mo–Mn_2 (dppf)	$[Mo(CO)_6]$ + MeCN at 80 °C + $[Mn_2(CO)_9(dppf\text{-}P)]$ (1:excess:2), thf + MeCN, 18%	2090m, 2009vw, 1993s, 1954w, 1933m, 1897m	7.39–7.26 (m, 30 H), 7.10–7.00 (m, 10 H), 4.36 (m, 4 H_b^{Mn}), 4.10 (m, 4 H^{Mo}), 3.99 (m, 4 H_a^{Mn}), 3.76 (m, 4 H^{Mo})[b,c]	65.6 (br s, Ph_2PMn), 26.8 (s, Ph_2PMo)[b,d]
Cr–W–Cr (dppf)	$[W(CO)_6]$ + Me_3NO in MeCN + $[Cr(CO)_5(dppf\text{-}P)]$ (1.0:2.6:1.6), thf + MeCN, 20%[i]	2063m, 2019w, 1984w, 1939s, 1888m	*j*	≈ 47 (s, br, Ph_2PCr)[l] 46.84 (s, Ph_2PCr),[b–l] 20.6 [t, Ph_2PW, *J*(PW) 244], 15.6 [t, Ph_2PW, *J*(PW) 282],
W–W–W (dppf)	$[W(CO)_6]$ + Me_3NO + dppf (1.0:0.8:0.4), thf + CH_2Cl_2, 1%	2071m, 2016w, 1982w, 1938vs, 1888s	7.37–7.32 (m, 40 H), 4.25 (m, 8 H^{W}), 4.09 (m, 4 $H_b^{W'}$), 3.95 (m, 4 $H_a^{W'}$)[m]	16.2 [t, Ph_2PW, *J*(PW) 283],11.2[t,Ph_2PW',*J*(PW) 249][m]
Mo–Cr–Mo (dppe)	$[Cr(CO)_6]$ + Me_3NO + $[Mo(CO)_5(dppe\text{-}P)]$ (1.5:1.5:1.0), thf, 8%	2072m, 2010vw, 1990w, 1947vs, 1885s	7.38–7.26 (m, 40 H), 2.25 (br s, 8 H)	66.34 (m, Ph_2PCr), 31.40 [(m, Ph_2PMo), $^2J(PP)$ 25, $^3J(PP)$ + $^5J(PP)$ 30]
Mo–Cr–Mo (dppp)	$[Cr(CO)_6]$ + Me_3NO + $[Mo(CO)_5(dppp\text{-}P)]$ (1.5:1.5:1.0), thf, 4%	2071m, 1988w, 1946vs, 1884s	7.32–7.30 (m, 40 H, Ph), 2.42 (m, 4 H, CH_2PPh_2Mo), 2.32 (m, 4 H, CH_2PPh_2Cr), 1.25 (m, 4 H, CH_2)	61.75 (s, Ph_2PCr),[l] 44, 71 (s, Ph_2PCr),[k] 26.67 (s, Ph_2PMo),[m] 26.97 (s, Ph_2PMo)[k]

[a] H_a and H_b refer to the external and internal phosphinocyclopentadienyl protons respectively; H^M denotes the protons of the metal co-ordinated (Cr, Mo, W, Fe or Mn) phosphinocyclopentadienyl ring; M = $[M(CO)_4]$, M′ = $[M(CO)_5]$. [b] In $CDCl_3$ (300 MHz). [c] Assignment is assisted by ^1H–^1H decoupling experiments and by comparison of shift values with those of $[M_y(CO)_x(dppf)]$ (M = Cr, Mo or W, *y* = 2, *x* = 10; M = Mn, *y* = 4, *x* = 18). [d] Peaks due to traces of the unidentate complex are observed. [e] Data not available. [f] In $CDCl_3$ (270 MHz); no decoupling analysis. [g] Quality of spectrum was poor. [h] Decoupling experiments were carried out but uninformative. [i] Product yield includes other contaminating by-products. [j] Peak assignment not feasible due to overlapping resonances from contaminating species. [k] Tentatively assigned as the *cis* isomer (minor component). [l] *trans* isomer. [m] In $CDCl_3$ (90 MHz). Assignment of peaks assisted by comparison with the ^1H shifts of the W–Cr–W complex.

$[M(CO)_5(PR_3)]$ decreases in the order W > Mo ⩾ Cr. This anomaly can be attributed to the rate-enhancing effect of a sterically bulky phosphine on a smaller chromium centre. A similar argument was put forward by Basolo and co-workers in explaining the faster rates shown by the bulkier ligands.

All the oligomers isolated can be treated as disubstituted tetracarbonyl complexes of a Group 6 metal with two long-chain metalloligands as substituents. The complexes of Cr and W are almost invariably *trans* while the molybdenum analogues are exclusively *cis*. Though the formation of a *trans* product from a *cis* precursor has some literature precedence,[13] steric factors alone clearly cannot explain the observed geometrical preference. We attribute this to the difference in behaviour in their five-co-ordinate intermediates. Stepwise substitution of *cis*-$[M(CO)_4(solv)_2]$ by the metalloligand (L) would immediately give *cis*-$[M(CO)_4L(solv)]$ which could lead to the final product through two mechanisms, dissociative S_N1 and associative S_N2.[14] Dissociation would give five-co-ordinate



Scheme 2 Structural representations of the heteropolymetallic oligomers

$[M(CO)_4L]$ which is known to be static for Mo,[15] with the bulky L occupying an equatorial position in a C_s tetragonal-pyramidal structure, but highly fluxional for W and Cr.[16] Entrance of a second L group thus gives a *cis* isomer to Mo and a statistical mixture of *trans* and *cis* for Cr and W. For steric reasons, the *trans* isomer for the latter metals is thermodynamically preferred. The alternative associative mechanism would also result in the *cis* isomer, provided the intramolecular ligand rearrangement is slow. The rate of this non-dissociative fluxional process has been found to decrease in the order Cr > W > Mo.[17] With Mo showing the greatest barrier for *cis* $\Leftrightarrow$ *trans* isomerisation, it is thus not surprising that the thermodynamically less favoured *cis* isomer is found. All the oligomers decompose readily in solutions. Such decomposition, which is electronically (*cis* labilisation) and entropically driven, releases the unidentate complex fragments. The highest instability is shown in the $[MoMn_4]$ complex, which is sterically most demanding, also suggests a steric contribution to such decomposition. The preference for the *cis*-molybdenum complexes to decompose rather than isomerise gives a clear indication of its much favoured dissociative phosphine loss with respect to isomerisation.

The asymmetric trimetallic complexes such as $[(OC)_5Mo(\mu\text{-}dppf)Mo(CO)_4(\mu\text{-}dppf)Cr(CO)_5]$ are not detected in any of the bimetallic syntheses. This further confirms that the bimetallics do not favour oxidative decarbonylation to give the trimetallics. Such attack, for example, on $[(OC)_5Mo(\mu\text{-}dppf)Cr(CO)_5]$ would have given the above trimetallic complex since Me_3NO is known to attack preferentially the molybdenum carbonyls.

Experimental

General.—All procedures were performed under pure dry argon using standard Schlenk techniques. The general procedures and instruments used followed those described earlier.[18] All NMR spectra were recorded on JEOL 90Q FT, Bruker 250 or AC 300F spectrometers; $^{31}P\text{-}\{^1H\}$ spectra were recorded at 36.23, 101.25 and 121.49 MHz respectively. 1,1′-Bis(diphenylphosphino)ferrocene (dppf) was synthesised according to a literature method[19] or obtained commercially. The complexes $[M(CO)_5(dppf\text{-}P)]$ (M = Cr, Mo or W), $[Fe(CO)_4(dppf\text{-}P)]$ and $[Mn_2(CO)_9(dppf\text{-}P)]$ were synthesised as previously described.[20] The complex *cis*-$[M(CO)_4(MeCN)_2]$ was generated from $[M(CO)_6]$ and $Me_3NO{\cdot}2H_2O$ at room temperature (r.t.) in MeCN under partial vacuum and used *in situ*. The reported yields are generally low because of competitive reactions.

The homometallic oligomers $[(OC)_5M(\mu\text{-}dppf)M(CO)_4(\mu\text{-}dppf)M(CO)_5]$ were obtained as trace to minor products in the Me_3NO-induced oxidative decarbonylation reaction of $[M(CO)_6]$ with dppf.[20a] The isomeric notation preceding the formula refers to the central tetracarbonylmetal group: *trans*-$[(OC)_5Cr(\mu\text{-}dppf)Cr(CO)_4(\mu\text{-}dppf)Cr(CO)_5]$ (Found: C, 59.20; H, 3.25; Cr, 9.40; Fe, 6.25; P, 7.70. Calc. for $C_{82}H_{56}Cr_3Fe_2O_{14}P_4$: C, 59.45; H, 3.40; Cr, 9.40; Fe, 6.75; P, 7.50%); *cis*-$[(OC)_5Mo(\mu\text{-}dppf)Mo(CO)_4(\mu\text{-}dppf)Mo(CO)_5]{\cdot}0.33C_6H_{14}$ (Found: C, 55.50; H, 3.30; Fe, 5.15; Mo, 14.90; P, 7.35. Calc. for $C_{84}H_{60.7}Fe_2Mo_3O_{14}P_4$: C, 55.50; H, 3.35; Fe, 6.15; Mo, 15.85; P, 6.80%); *trans*-$[(OC)_5W(\mu\text{-}dppf)W(CO)_4(\mu\text{-}dppf)W(CO)_5]{\cdot}0.5C_6H_{14}$ (Found: C, 48.95; H, 3.10; Fe, 4.80; P, 5.85; W, 25.55. Calc. for $C_{85}H_{63}Fe_2O_{14}P_4W_3$: C, 48.70; H, 3.05; Fe, 5.35; P, 5.90; W, 26.30%).

trans-$[(OC)_5Mo(\mu\text{-}dppf)Cr(CO)_4(\mu\text{-}dppf)Mo(CO)_5]$. This is a typical synthesis of a bimetallic complex in which the trimetallic (or a higher homologue) is isolated as a minor product. Solid $[Mo(CO)_5(dppf\text{-}P)]$ (0.201 g, 0.23 mmol) was added to a yellow mixture of $[Cr(CO)_6]$ (0.078 g, 0.35 mmol) and Me_3NO (0.037 g, 0.33 mmol) which had been stirring in tetrahydrofuran (thf) (40 cm^3) for 15 min at 25 °C. The resultant orange-yellow solution was stirred for 3 h, after which it was filtered and the solvent removed *in vacuo*. The products were separated by preparative TLC using 15% CH_2Cl_2 in hexane solution as the eluent. The elution order followed the general sequence of $[Cr(CO)_5(NMe_3)]$ (bright yellow) > M = Cr, M′ = Mo bimetallic complex (orange) > M = Cr, M′ = Mo oligomer (orange yellow) > $[Mo(CO)_5(dppfo\text{-}P)]$ (orange-brown) (on baseline). Further recrystallisation from a CH_2Cl_2–hexane mixture yielded the orange complex $[(OC)_5Cr(\mu\text{-}dppf)Mo(CO)_5]{\cdot}0.5CH_2Cl_2$ (0.082 g, 33%)[4c] together with an orange minor product, *trans*-$[(OC)_5Mo(\mu\text{-}dppf)Cr(CO)_4(\mu\text{-}dppf)Mo(CO)_5]$ (0.033 g, 15%) (Found: C, 56.35; H, 3.10; Cr, 2.90; Fe, 6.40; Mo, 10.55; P, 7.40. Calc. for $C_{85}H_{56}CrFe_2Mo_2O_{14}P_4$: C, 56.45; H, 3.25; Cr, 3.00; Fe, 6.40; Mo, 11.00; P, 7.10%), $\{^{13}C\text{-}\{^1H\}$ NMR ($CDCl_3$): δ 223.1 [t, *J*(CP) 12.8], 210.0 [d, *J*(CP) 22.6] and 205.7 [d, *J*(CP) 8.3 Hz]$\}$ and $[Mo(CO)_5(dppfo\text{-}P)]$ (0.042 g, 21%). (Found: C, 58.25; H, 3.55; Fe, 6.40; Mo, 11.35; P, 7.95. Calc. for $C_{39}H_{28}FeMoO_6P_2$: C, 58.10; H, 3.50; Fe, 6.95; Mo, 11.90; P, 7.70%) [ν_{max}(CO) 2072m, 1991w and 1947s(br) cm^{-1} ($CHCl_3$); $\delta_H(CDCl_3)$ 7.67–7.31 (m, 20 H, Ph), 4.80 (m, 2 H_b^{PO}), 4.30 (q, 2 H_b^{Mo}), 4.18 (q, 2 H_a^{PO}) and 4.04 (1, 2 H_a^{Mo}); $\delta_P(CDCl_3)$ 28.81 (s, 1 P^{PO}) and 28.40 (s, 1 P^{Mo})].

The dppfo complexes of Cr and W also formed under similar conditions when $[M(CO)_5(dppf\text{-}P)]$ (M = Cr or W) respectively were used as the substrates. $[Cr(CO)_5(dppfo\text{-}P)]{\cdot}2H_2O$ (Found: C, 58.50; H, 3.70; Cr, 5.70; Fe, 6.80; P, 7.60. Calc. for

$C_{39}H_{32}CrFeO_8P_2$ C, 58.65; H, 4.05; Cr, 6.50; Fe, 7.00; P, 7.75%); ν_{max}(CO) 2063m, 1984w, and 1940s(br) cm^{-1} ($CHCl_3$); δ_H ($CDCl_3$, 90 MHz) 7.67–7.27 (m, 20 H, Ph), 4.80 (m, 2 H_b^{PO}), 4.27 (q, 2 H_b^{Cr}), 4.20 (q, 2 H_a^{PO}), and 4.04 (q, 2 H_a^{Cr}); δ_P($CDCl_3$, 90 MHz) 47.25 (s, 1 P^{Cr}) and 28.81 (s, 1 P^{PO}); $[W(CO)_5$(dppfo-*P*)] (Found: C, 52.45; H, 3.05; Fe, 5.90; P, 6.80; W, 14.40. Calc. for $C_{39}H_{28}FeO_6P_2W$: C, 52.40; H, 3.15; Fe, 6.25; P, 6.95; W, 20.55%); ν_{max}(CO) 2071m, 1983w and 1941s cm^{-1} ($CHCl_3$); δ_H($CDCl_3$) 7.67–7.32 (m, 20 H, Ph), 4.83 (m, 2 H_b^{PO}), 4.30 [q, 2 H_b^{W}, *J*(P–H) 1.3], 4.18 [q, 2 H_a^{PO}, *J*(P–H) 2.1] and 4.04 [q, 2 H_a^{W}, *J*(P–H) 1.6]; δ_P($CDCl_3$) 28.81 (s, 1 P^{PO}) and 11.17 [t, 1 P^{W}, *J*(W–P) 249 Hz].

trans-$[(OC)_5W(\mu\text{-dppf})Cr(CO)_4(\mu\text{-dppf})W(CO)_5]$.—Substrate: $[Cr(CO)_6]$ + Me_3NO + $[W(CO)_5$(dppf-*P*)] (1.4 : 1.3 : 1). Reaction duration: 2 h. Yield: 4% (Found: C, 50.90; H, 2.70; Cr, 2.80; Fe, 5.65; P, 6.25; W, 17.30. Calc. for $C_{82}H_{56}CrFe_2O_{14}P_4W_2$: C, 51.30; H, 2.95; Cr, 2.70; Fe, 5.80; P, 6.45; W, 19.15%).

trans-$[(OC)_4Fe(\mu\text{-dppf})Cr(CO)_4(\mu\text{-dppf})Fe(CO)_4]$. Yield: 3%. This complex has been characterised only by ^{1}H and ^{31}P-{^{1}H} NMR spectroscopy, while *trans*-$[(OC)_5Mn\text{–}Mn(CO)_4(\mu\text{-dppf})Cr(CO)_4(\mu\text{-dppf})(OC)_4Mn\text{–}Mn(CO)_5]$ (yield 3%) has been identified by its IR and ^{31}P-{^{1}H} NMR spectra. These spectroscopic data are summarised in Table 1. The yield was too low to allow for an accurate elemental analysis.

cis-$[(OC)_4Fe(\mu\text{-dppf})Mo(CO)_4(\mu\text{-dppf})Fe(CO)_4]\cdot 0.75CH_2Cl_2$. Substrate: $[Mo(CO)_6]$ + Me_3NO + $[Fe(CO)_4$(dppf-*P*)] (1.4 : 1.3 : 1). Duration: 3 h: Yield: 6% (Found: C, 56.65; H, 3.35; Fe, 12.55; Mo, 6.35; P, 6.90, Calc. for $C_{80.8}H_{57.5}Cl_{1.5}Fe_4MoO_{12}P_4$: C, 56.50; H, 3.40; Fe, 13.00; Mo, 5.60; P, 7.20%). This complex could also be produced from a designed synthesis as described below.

Designed Syntheses.—*cis*-$[(OC)_xM(\mu\text{-dppf})Mo(CO)_4(\mu\text{-dppf})M(CO)_x]$ (M = Cr, *x* = 5; M = Fe, *x* = 4). The compound $[Mo(CO)_6]$ (0.018 g, 0.07 mmol) was mixed with Me_3NO (0.015 g, 0.13 mmol, M = Cr; 0.019 g, 0.17 mmol, M = Fe) in MeCN (20 cm^3) for 2 h at 25 °C. In the course of the reaction a slight vacuum was applied to remove the liberated CO_2 and NMe_3. The yellowish green solution formed was transferred dropwise under argon into a thf solution (15 cm^3) of $[M(CO)_x$(dppf-*P*)] (0.100 g) *via* a Teflon tube. The orange-yellow solution was stirred overnight (21 h for M = Cr, 19 h for M = Fe). Isolation of products was achieved by preparative TLC using an eluent mixture of 20–25% CH_2Cl_2 in hexane. In this reaction, unreacted unidentate complex $[M(CO)_x$(dppf-*P*)] was always isolated. The other products obtained were $[(OC)_5Cr(\mu\text{-dppf})Mo(CO)_5]$ (0.025 g, 22%) and *cis*-$[(OC)_5Cr(\mu\text{-dppf})Mo(CO)_4(\mu\text{-dppf})Cr(CO)_5]\cdot 0.75C_6H_{14}$ (0.018 g, 18%) (Found: C, 58.85; H, 3.85; Cr, 5.65; Fe, 6.30; Mo, 5.50; P, 7.45. Calc. for $C_{86.5}H_{66.5}Cr_2Fe_2MoO_{14}P_4$: C, 58.85; H, 3.80; Cr, 5.90; Fe, 6.35; Mo, 5.45; P, 7.00%) for the M = Cr reaction. In the case of M = Fe, *cis*-$[(OC)_4Fe(\mu\text{-dppf})Mo(CO)_4(\mu\text{-dppf})Fe(CO)_4]$ (0.008 g, 9%) was isolated together with a trace quantity of $[(OC)_4Fe(\mu\text{-dppf})Mo(CO)_4]$ and some unidentified products.

cis-$[(OC)_5Mn\text{–}Mn(CO)_4(\mu\text{-dppf})Mo(CO)_4(\mu\text{-dppf})(OC)_4Mn\text{–}Mn(CO)_5]$. The compound $[Mo(CO)_6]$ (0.017 g, 0.06 mmol) was refluxed in MeCN (20 cm^3) for 2 h, after which the IR spectrum of the mixture was taken to ensure that most of the substrate had been converted into *cis*-$[Mo(CO)_4(MeCN)_2]$. The solution was cooled to r.t. and transferred dropwise to a thf solution (20 cm^3) of $[Mn_2(CO)_9$(dppf-*P*)] (0.100 g, 0.11 mmol). The resultant solution was stirred overnight (17 h), after which the solvent was removed *in vacuo*. The residue was redissolved in CH_2Cl_2, applied to TLC plates and eluted with 25% CH_2Cl_2 in hexane solution. Extraction followed by recrystallisation from a CH_2Cl_2–MeOH mixture yielded *cis*-$[(OC)_5Mn\text{–}Mn(CO)_4(\mu\text{-dppf})Mo(CO)_4(\mu\text{-dppf})(OC)_4Mn\text{–}Mn(CO)_5]$ (0.019 g, 18%) (Found: C, 52.85; H, 2.75; Fe, 5.05; Mn, 10.35; Mo, 4.75; P, 5.95. Calc. for $C_{90}H_{56}Fe_2Mn_4MoO_{22}P_4$: C, 52.95; H, 2.75; Fe, 5.45; Mn, 10.75; Mo, 4.70; P, 6.05%), a trace quantity of $[(OC)_5Mo(\mu\text{-dppf})Mn_2(CO)_9]$, and some unreacted unidentate complex $[Mn_2(CO)_9$(dppf-*P*)] (0.007 g).

$[(OC)_5Cr(\mu\text{-dppf})W(CO)_4(\mu\text{-dppf})Cr(CO)_5]$. This complex was prepared in general as for the MoM_2 complex above. Both *cis* and *trans* isomers of $[(OC)_5Cr(\mu\text{-dppf})W(CO)_4(\mu\text{-dppf})Cr(CO)_5]$ (0.017 g) were formed from $[W(CO)_6]$ (0.030 g, 0.09 mmol), Me_3NO (0.025 g, 0.22 mmol) and $[Cr(CO)_5$(dppf-*P*)] (0.100 g, 0.13 mmol). Besides the unreacted $[Cr(CO)_5$(dppf-*P*)] (0.030 g), some unidentified by-products were detected. An accurate microanalysis was not feasible.

trans-$[(OC)_5Mo(\mu\text{-dppe})Cr(CO)_4(\mu\text{-dppe})Mo(CO)_5]$.—This complex was prepared as described above for the dppf complex. Yield: 0.012 g, 8% from $[Cr(CO)_6]$ (0.052 g, 0.24 mmol) and $[Mo(CO)_5$(dppe-*P*)] (0.100 g, 0.16 mmol) (Found: C, 55.20; H, 3.40; Cr, 3.25; Mo, 13.45; P, 9.00. Calc. for $C_{66}H_{48}CrMo_2O_{14}P_4$: C, 55.30; H, 3.35; Cr, 3.65; Mo, 13.40; P, 8.65%). The complex *trans*-$[(OC)_5Mo(\mu\text{-dppp})Cr(CO)_4(\mu\text{-dppp})Mo(CO)_5]$ was prepared similarly. Yield: 0.007 g, (4%) (Found: C, 55.85; H, 3.60%. Calc. for $C_{68}H_{52}CrMo_2O_{14}P_4$: C, 55.90; H, 3.55).

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