Inorg. Chem. **1990**, *29*, 1181-1186

Fourier synthesis. Block-diagonal least-squares refinement for all of the 71 non-hydrogen atoms with anisotropic temperature factors converged to $R = 0.105$. Addition of calculated hydrogen atoms with isotropic thermal parameters to the refinement gave the final R values, $R = 0.091$ and $R_w = 0.088$ (weighting scheme: $1/w = \sigma^2 + (0.015|F_o|)^2$). The UNICS III computer program system at the Institute for Molecular Science (IMS) was used throughout.

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Supplementary Material Available: Tables SI and SII, listing atomic positional parameters and anisotropic temperature factors (3 pages); listings of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

Contribution from the Laboratoire de Chimie de Coordination, associé au CNRS (UA 416), Université Louis Pasteur, F-67070 Strasbourg Cédex, France

Stepwise Synthesis and Reactivity of $Ph_2PCH_2PPh_2$-Stabilized Mixed-Metal Clusters Containing Three or Four Different Metals

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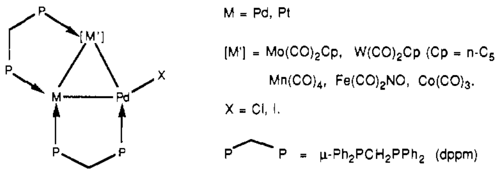
The reactions of the carbonylmetalate anions $[m]^- = [Co(CO)_4]^-$, $[Fe(CO)_3NO]^-$, $[Mn(CO)_5]^-$, $[Mo(CO)_3Cp]^-$, and $[W(CO)_3Cp]^-$ with the trinuclear clusters $[PdMCoX(CO)_3(dppm)_2]$ (M = Pd, Pt; X = Cl, I; dppm = μ-$Ph_2PCH_2PPh_2$), $[Pd_2FeI(CO)_2NO(dppm)_2]$, $[Pd_2MnCl(CO)_4(dppm)_2]$, $[PdMMoCpCl(CO)_2(dppm)_2]$, and $[PdMWCpCl(CO)_2(dppm)_2]$ occur by substitution of the Pd-bound halide by the carbonylmetalate anions. As a result of Pd–m bond formation, they afford $[Pd_2Co_2(CO)_7(dppm)_2]$ (**3a**), $[Pd_2Mn_2(CO)_9(dppm)_2]$ (**10**), and new tetranuclear clusters $[PdMCoFe(CO)_6(NO)(dppm)_2]$ (M = Pd, **4a**; M = Pt, **4b**), $[PdMCoMn(CO)_8(dppm)_2]$ (M = Pd, **5a**; M = Pt, **5b**), $[PdPtCoMoCp(CO)_6(dppm)_2]$ (**6b**), $[Pd_2FeCo(CO)_6(NO)(dppm)_2]$ (**8**), $[PdMMoCoCp(CO)_6(dppm)_2]$ (M = Pd, **13a**; M = Pt, **13b**), and $[Pd_2WCoCp(CO)_6(dppm)_2]$ (**14**). These clusters possess a metalloligated triangular framework PdMM′m, with three (M = Pd) or four (M = Pt) different metals, the Pd, M, and M′ atoms constituting the triangle and m belonging to the metalloligand. The stepwise syntheses used in this work have led to the isolation of two pairs of positional isomers: $[PdPtCoMoCp(CO)_6(dppm)_2]$ (**6b**), $[PdPtMoCoCp(CO)_6(dppm)_2]$ (**13b**) and $[Pd_2CoFe(CO)_6(NO)(dppm)_2]$ (**4a**), $[Pd_2FeCo(CO)_6(NO)(dppm)_2]$ (**8**), respectively, which do not interconvert and present interesting spectroscopic (IR, NMR) features. The substitution of the halide of $[PdMCoX(CO)_3(dppm)_2]$ was shown to depend on the nature of (i) the halide (Cl vs I), (ii) the incoming carbonylmetalate anion $[m]^-$, and (iii) the solvent used for the reaction. The lability of the exocyclic Pd–m bond has been studied with respect to the nature of both the endocyclic metals (Pd, M, and M′) and the exocyclic metal m. These studies reveal that (i) the space available for coordination at the Pd center decreases in the order $[M'] = Co(CO)_3 \gg Mo(CO)_2Cp$, (ii) the Pd–m bond is less labile when M = Pd than when M = Pt, and (iii) the steric hindrance of the metalloligand increases in the sequence of m = $Co(CO)_4 \leq Fe(CO)_3NO \ll Mn(CO)_5 \ll Mo(CO)_3Cp \approx W(CO)_3Cp$.

Introduction

In previous papers, we have described the syntheses of molecular mixed-metal clusters whose structures are characterized by a triangular metal core of which two edges are bridged by a $Ph_2PCH_2PPh_2$ (dppm) ligand.[1-3] Among them, clusters containing a halide ligand are of particular interest as potential precursors of higher nuclearity clusters, e.g., by substituting the halide with various carbonylmetalate anions.



This would, in principle, allow the systematic access to tetranuclear metalloligated clusters, containing three (M = Pd) or four (M = Pt) different metal atoms, stabilized by dppm ligands. Other methods have led to systematic syntheses of multimetallic clusters.[4] We describe in this paper comparative studies on the reactivity of various carbonylmetalates toward such halogeno clusters as a function of the nature of their constitutive metals. A preliminary communication on part of this work has appeared.[3a]

Results

Syntheses. In order to facilitate comparisons between related molecules, these will be presented according to the nature of their triangular core PdMM′. For clarity, the metal carbonyl fragments are written in square brackets, e.g. [M′] and [m], and the corresponding metal atoms without.

1. Clusters with a PdMCo Core (M = Pd, Pt). The red-brown trinuclear cluster $[Pd_2CoCl(CO)_3(dppm)_2]$ (**1a**) reacts immediately with 1 equiv of $Na[Co(CO)_4]$ in solvents such as THF or Et_2O, to give quantitative yields of the deep green tetranuclear cluster $[Pd_2Co_2(CO)_7(dppm)_2]$ (**3a**) (eq 1) whose crystal structure has been determined previously.[1a,b] When the reaction of eq 1 is carried out with $K[Fe(CO)_3NO]$, $Na[Mn(CO)_5]$, or $Na[Mo(CO)_3Cp]$, it affords the new tetranuclear clusters $[PdMCoFe(CO)_6(NO)(dppm)_2]$ (**4a**, M = Pd; **4b**, M = Pt), $[PdMCoMn(CO)_8(dppm)_2]$ (**5a**, M = Pd; **5b**, M = Pt), or [PdMCoMoCp-

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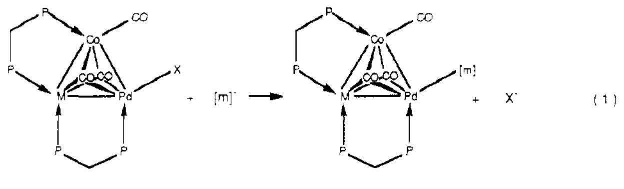
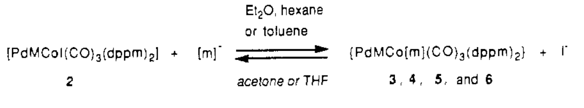


(1)

(**1a**) M = Pd, (**1b**) M = Pt; X = Cl
(**2a**) M = Pd, (**2b**) M = Pt; X = I
(**3a**) M = Pd, (**3b**) M = Pt; [m] = Co(CO)$_4$
(**4a**) M = Pd, (**4b**) M = Pt; [m] = Fe(CO)$_3$NO
(**5a**) M = Pd, (**5b**) M = Pt; [m] = Mn(CO)$_5$
(**6a**) M = Pd, (**6b**) M = Pt; [m] = Mo(CO)$_3$Cp

(CO)$_6$(dppm)$_2$] (**6a**, M = Pd; **6b**, M = Pt), respectively. They have been characterized by IR and ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. The data are typical for this family of (dppm)$_2$-substituted clusters and are consistent with the proposed structures (see Experimental Section and Tables I and II). Whereas solutions of **3a** are stable under nitrogen, THF solutions of **4a** slowly turned brown with formation of an insoluble material. The manganese-ligated clusters **5** (M = Pd, Pt) are even more unstable and reacted during the recording of their NMR spectra in CDCl$_3$ with formation of [PdMCoCl(CO)$_3$(dppm)$_2$] (**1**). It should be noted that the substitution reactions of the chloride in **1a** by the carbonylmetalate anions are irreversible in, e.g., Et$_2$O or THF and that the corresponding substitutions of the iodide in [Pd$_2$CoI(CO)$_3$(dppm)$_2$] (**2a**) are quantitative and immediate in Et$_2$O despite its low solubility in this solvent. This contrasts with the corresponding reactions of **2a** in THF,[1b,c] where they are incomplete and slower, although addition of an excess of the carbonylmetalates drives the reactions toward the characteristic green color of the tetranuclear clusters. Formation of the latter can also be achieved by evaporation of the THF solution to dryness and subsequent extraction with Et$_2$O or toluene. Addition of an equal volume of THF to a Et$_2$O reaction mixture of, e.g., **5a**, causes reversal of the reaction back to **2a**. These solvent effects, most notable in the case of the iodo derivatives, are summarized in eq 2. When [Pd$_2$CoCl(CO)$_3$(dppm)$_2$] is reacted with [Mo(CO)$_3$Cp]$^-$, a rapid color change occurs, again more readily in Et$_2$O than in THF. The reaction probably leads to the tetranuclear cluster [Pd$_2$CoMoCp(CO)$_6$(dppm)$_2$] (**6a**), which, however, could not be isolated pure in the solid state but, upon workup, reverted back to the starting materials (IR evidence). However, the use of a slightly different workup, i.e. extraction with toluene, allows isolation of clusters **6** from the reaction of **1** with [Mo(CO)$_3$Cp]$^-$ in THF. Green solutions of **6** in toluene should be kept at −20 °C because of progressive transformation (1 day, 25 °C) into red solutions, which after replacement of toluene with CH$_2$Cl$_2$/CDCl$_3$ were shown to contain only [PdMCoCl(CO)$_3$(dppm)$_2$] (M = Pd, Pt). Interestingly, the instability of **6** appears to correlate with the highly solvent-dependent lability of its exocyclic Pd–Mo bond. We shall return to this point later in the Discussion. In contrast to clusters **3**, **6b** reacts with CO in THF to afford a mixture of [PdPtCo(CO)$_4$(dppm)$_2$][Mo(CO)$_3$Cp] and **6b** in a ca. 1:6 ratio. Cluster **6a** also reacts with CO, affording [Pd$_2$Co(CO)$_4$(dppm)$_2$][Mo(CO)$_3$Cp] and **6a** in a smaller ratio than for **6b**, showing a "platinum effect" on the lability of the exocyclic Pd–Mo bond in clusters **6**.[1b,c]

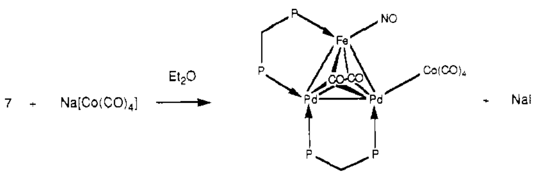


$$\underset{2}{[\mathrm{PdMCoI(CO)_3(dppm)_2}]} + [\mathrm{m}]^- \xrightleftharpoons[\text{acetone or THF}]{\mathrm{Et_2O},\ \text{hexane or toluene}} \underset{3,\ 4,\ 5,\ \text{and}\ 6}{[\mathrm{PdMCo[m](CO)_3(dppm)_2}]} + \mathrm{I}^- \quad (2)$$

The cluster [PdPtCoI(CO)$_3$(dppm)$_2$] (**2b**) is a stable and convenient precursor for the stepwise synthesis of clusters containing four different metal atoms. Thus, it reacts with K[Fe(CO)$_3$NO] or Na[Mn(CO)$_5$] in Et$_2$O, to afford **4b** or **5b**, respectively (eq 1). The reactions are quantitative in Et$_2$O whereas in THF no reaction takes place because of the tendency, independently checked, for **4b** and **5b** to revert back to **2b** when iodide ions are present. This tendency appears even more pronounced than in the case of the analogous clusters **4a** and **5a**. However, **4b** or **5b** can be dissolved in pure THF without significant dissociation, as shown, e.g., by their IR spectrum in this solvent and the characteristic blue-green color of their solutions.

In order to compare the preference of closely related cationic clusters of core composition Pd$_2$Co and PdPtCo for binding carbonylmetalates, the clusters [Pd$_2$Co(THF)(CO)$_3$(dppm)$_2$][PF$_6$] and [PdPtCo(THF)(CO)$_3$(dppm)$_2$][PF$_6$][1c] in an equimolar mixture were allowed to compete with 1 equiv of [Co(CO)$_4$]$^-$ (THF, 25 °C, 2 h). The red solution turned green, and the ^{31}P NMR analysis of the mixture revealed the presence of [Pd$_2$Co$_2$(CO)$_7$(dppm)$_2$] (**3a**) and [PdPtCo$_2$(CO)$_7$(dppm)$_2$] (**3b**) in a 2:1 ratio.

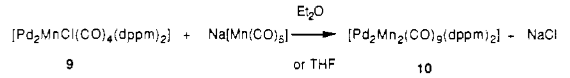
2. Clusters with a Pd$_2$Fe Core. The red-brown cluster [Pd$_2$FeI(CO)$_2$NO(dppm)$_2$] (**7**)[2b] reacts with Na[Co(CO)$_4$] in Et$_2$O, yielding dark green **8** in 94% yields (eq 3). It is noteworthy that **8** and **4a** are structural isomers; however, they can be easily differentiated by IR and NMR spectroscopy (Tables I and II). Cluster **8** does not react with a large excess of [Co(CO)$_4$]$^-$, indicating that the endocyclic Fe(CO)$_2$NO fragment is not exchanged for the isoelectronic Co(CO)$_3$ fragment. On the other hand, that the iodide ligand of **7** is not replaced by [W(CO)$_3$Cp]$^-$ in Et$_2$O may be related to the lability of the exocyclic Pd–Mo bond as noted for **6**.



(3)

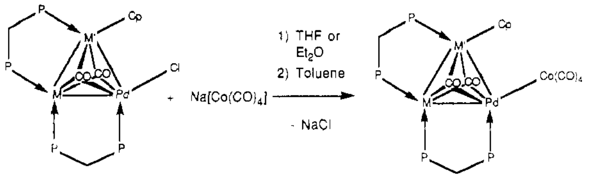
8

3. Clusters with a Pd$_2$Mn Core. Stable [Pd$_2$MnCl(CO)$_4$(dppm)$_2$] (**9**)[2b] reacts with Na[Mn(CO)$_5$] in THF to afford the crystallographically characterized tetranuclear, metalloligated cluster [Pd$_2$Mn$_2$(CO)$_9$(dppm)$_2$] (**10**)[2] in 82% yield (eq 4). Cluster **10** is fairly unstable, and this preparation has the advantage of requiring a simpler workup than the direct synthesis consisting of the reaction of [Pd$_2$Cl$_2$(dppm)$_2$] with 2 equiv of Na[Mn(CO)$_5$].[2b]



$$\underset{9}{[\mathrm{Pd_2MnCl(CO)_4(dppm)_2}]} + \mathrm{Na[Mn(CO)_5]} \xrightarrow[\text{or THF}]{\mathrm{Et_2O}} \underset{10}{[\mathrm{Pd_2Mn_2(CO)_9(dppm)_2}]} + \mathrm{NaCl} \quad (4)$$

4. Clusters with a PdMMo (M = Pd, Pt) or Pd$_2$W Core. The violet clusters [PdMM′CoCp(CO)$_6$(dppm)$_2$] (M = Pd, M′ = Mo, **13a**; M = Pt, M′ = Mo, **13b**; M = Pd, M′ = W, **14**) are prepared in good yields from [PdMM′ClCp(CO)$_2$(dppm)$_2$] (**11a**, **11b**, **12**), respectively (eq 5). Whereas with [Co(CO)$_4$]$^-$ the reaction is complete even in THF, mixtures of [PdMM′Cp(THF)(CO)$_2$(dppm)$_2$][M′(CO)$_3$Cp] and [PdMM′$_2$Cp$_2$(CO)$_5$(dppm)$_2$] are observed with [M′(CO)$_3$Cp]$^-$. However, the pure metalloligated clusters may be isolated upon extraction with toluene.[3c] Therefore, these reactions should be, in general, carried out in THF or Et$_2$O, followed by extraction with toluene. In order to compare the lability of the exocyclic Pd–Co bond in **13b** vs **3b**, the former cluster was dissolved in THF and carbon monoxide was bubbled through the solution. The brown-violet color of the solution turned immediately to light orange-brown, and the IR spectrum of the reaction mixture showed absorption bands at 2041 (w), 1887 (vs), and 1792 (w) cm^{-1}, corresponding to the ion pair [PdPtMoCp(CO)$_3$(dppm)$_2$][Co(CO)$_4$]. The same behavior is observed with **13a**. Dissociation of the Pd–Co bond in **13b** is also observed in weak donor solvents like acetone (although not as extensively as



(5)

(**11a**) M = Pd, M′ = Mo
(**11b**) M = Pt, M′ = Mo
(**12**) M = Pd, M′ = W
(**13a**) M = Pd, M′ = Mo
(**13b**) M = Pt, M′ = Mo
(**14**) M = Pd, M′ = W

Table I. Infrared Data for the Tetranuclear Clusters

complex	no.	ν(CO), cm^{-1} [a]	ν(NO), cm^{-1} [a]
$[Pd_2Co_2(CO)_7(dppm)_2]$	**3a**	2009 (vs), 1985 (s), 1924 (vs), 1896 (vs), 1879 (vs)	
$[Pd_2CoFe(CO)_6(NO)(dppm)_2]$	**4a**	1998 (vs), 1965 (s), 1908 (s), 1879 (s)	1688 (vs)
$[PdPtCoFe(CO)_6(NO)(dppm)_2]$	**4b**	2004 (vs), 1957 (s), 1875 (vs, br)	1670 (s)
$[Pd_2CoMn(CO)_8(dppm)_2]$	**5a**	2027 (vs), 1981 (s), 1935 (vs), 1909 (vs)	
$[PdPtCoMn(CO)_8(dppm)_2]$	**5b**	2022 (vs), 1991 (s), 1924 (vs), 1892 (vs)	
$[Pd_2CoMo(CO)_6Cp(dppm)_2]$	**6a**[b]	2003 (s), 1982 (m), 1901 (vs), 1874 (sh), 1857 (m), 1807 (m), 1791 (m)	
$[PdPtCoMo(CO)_6Cp(dppm)_2]$	**6b**[b]	2013 (vs), 1996 (m), 1903 (vs), 1876 (sh), 1858 (m), 1802 (m), 1779 (m)	
$[Pd_2FeCo(CO)_6(NO)(dppm)_2]$	**8**	2006 (vs), 1932 (s), 1902 (s), 1828 (m)	1730 (s)
$[Pd_2Mn_2(CO)_9(dppm)_2]$	**10**	2028 (vs), 1973 (s), 1927 (s), 1899 (vs), 1830 (w), 1780 (w)	
$[Pd_2MoCoCp(CO)_6(dppm)_2]$	**13a**[b]	2004 (vs), 1932 (s), 1914 (sh), 1888 (m, br), 1808 (w), 1763 (m, br)	
	13a[c]	2000 (vs), 1926 (s), 1886 (s), 1808 (w), 1766 (m, br)	
$[PdPtMoCoCp(CO)_6(dppm)_2]$	**13b**	1997 (s), 1907 (s, br), 1882 (s, br), 1776 (sh), 1764 (m, br)	
	13b[b]	2004 (vs), 1928 (vs), 1910 (w), 1881 (m), 1807 (w), 1764 (w)	
	13b[c]	2001 (vs), 1921 (vs), 1884 (vs), 1812 (w), 1772 (m, br)	
$[Pd_2WCoCp(CO)_6(dppm)_2]$	**14**	1994 (vs), 1913 (s), 1877 (s), 1753 (m)	

[a] Recorded in KBr unless otherwise stated; Abbreviations: w = weak, vs = very strong, s = strong, m = medium, sh = shoulder, br = broad. [b] Recorded in toluene. [c] Recorded in THF.

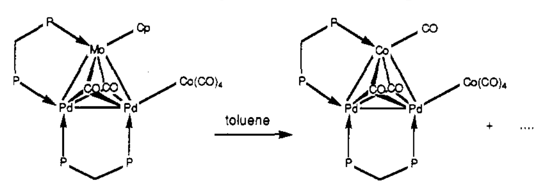
Table II. $^{31}P\{^1H\}$ NMR Data for the Tetranuclear Clusters[a]

		δ, ppm				J(P–P), Hz					
complex	no.	P(4)	P(3)	P(2)	P(1)	J(1–2)	J(1–3)	J(1–4)	J(2–3)	J(2–4)	J(3–4)
$[Pd_2Co_2(CO)_7(dppm)_2]$	**3a**	28.0[b]	−3.2	−10.9	−0.93	119	22	142	55	36	12
$[Pd_2CoFe(CO)_6(NO)(dppm)_2]$	**4a**	27.8[b]	−2.4	−7.7	−2.93	116	14	≈135[c]	58	92	≤10
$[Pd_2CoMn(CO)_8(dppm)_2]$	**5a**	34.0[b]	−2.3	4.3	−3.70	78.5	28	164	48	27	≈15[c]
$[PdPtCoMn(CO)_8(dppm)_2]$	**5b**[d]	23.0[b]	10.1	0.3	−3.87	96.5	17	126	18	32	≤10
$[Pd_2CoMo(CO)_6Cp(dppm)_2]$	**6a**[d,e]	32.8[b]	3.3	−1.93	−1.56	112.5	−29	178	56	28.5	−20.5
$[PdPtCoMo(CO)_6Cp(dppm)_2]$	**6b**	28.0	12.5	7.2	1.5	125	19	162	11	33.5	≤10
$[Pd_2FeCo(CO)_6(NO)(dppm)_2]$	**8**	42.1	3.8	−7.6	5.16	92	24	101	54	52	25
$[Pd_2MoCo(CO)_6Cp(dppm)_2]$	**13a**[e]	53.6	2.7	0.2	−4.4	107	50	26	67	82	25
$[PdPtMoCo(CO)_6Cp(dppm)_2]$	**13b**[d,e]	49.0	19.3	15.5	−9.1	96	39	31	20	72	24
$[Pd_2WCo(CO)_6Cp(dppm)_2]$	**14**	15.5	−7.5	−4.6	−20.5	98	50.5	22	68	79	22

[a] Recorded in toluene/toluene-d_8 unless otherwise stated. For phosphorus assignments, see text. [b] Broadened signal owing to the high quadrupolar moment of the cobalt atom. [c] Not accurately determined due to overlaping of signals of P(1) and P(3) and insufficient spectral resolution. [d] Coupling with ^{195}Pt in Hz: ^1J[Pt–P(1)] = 63 (**6b**), 41 (**13b**); ^1J[Pt–P(2)] = 3185 (**5b**), 3105 (**6b**), 3218.5 (**13b**); ^1J[Pt–P(3)] = 3981 (**5b**), 4091 (**6b**), 3781 (**13b**); ^1J[Pt–P(4)] = 84 (**13b**). [e] Recorded in toluene with a capillary containing D_2O as internal lock.

under CO bubbling), probably leading to the formation of the ion pair $[PdPtMoCp(acetone)(CO)_2(dppm)_2][Co(CO)_4]$, while some **13b** remains nondissociated (IR evidence). A similar Pd–Co bond dissociation is observed with **13a** in acetone although seemingly to a lesser extent than for **13b** (IR evidence). Such a "platinum effect" has been mentioned previously in related clusters.[1b,c]

In contrast to **13b**, a violet toluene solution of **13a** slowly turns green upon standing at room temperature (see Experimental Section). The major product (ca. 80% based on Co and IR and ^{31}P NMR evidence) is **3a**, showing that metal exchange, i.e. $Mo(CO)_2Cp$ for $Co(CO)_3$, has occurred (eq 6).



(6)

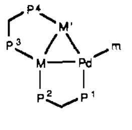
13a 3a

Spectroscopic Properties

IR spectroscopy in the 2100–1650-cm^{-1} region provides a good "fingerprint" of the tetrametallic clusters (Table I). Generally, their spectra can be interpreted as composed of the absorption bands typical of the trinuclear core and of those of the metalloligand [m]. This is well illustrated in the case of isomers **8** and **4a**, in which the nitrosyl ligand exhibits a vibration at 1688 cm^{-1} when coordinated to the endocyclic iron atom in **8** and at 1730 cm^{-1} when coordinated to the exocyclic iron atom in **4a**. The former value is very close to those found for $[Fe(CO)_3(NO)]^-$ (1635 and 1615 cm^{-1}),[5] and this reflects the electronegative character of the exocyclic metal center and thus the polarization of the $Pd^{\delta+}$–$Fe^{\delta-}$ exocyclic bond in **4a**. However, it is less clear for isomers **6b** and **13b**, for which numerous carbonyl vibrations are observed in the range 2000–1760 cm^{-1}, precluding an unambiguous assignment to the exocyclic vs endocyclic carbonyls. Thus caution must be taken in attributing the respective positions of the metal fragments in these isomers when one uses solely IR spectroscopy.

The ^{1}H NMR spectra of all these clusters show two distinct methylene groups, one for the dppm bridging the M–Pd bond (high-field triplet) and the other for the dppm bridging the M–M′ bond (low-field triplet) (see Experimental Section). The latter is sometimes further split by a small coupling constant, as previously seen for this family of compounds.[1c,2b,3c] It is noteworthy that changing the nature of the metal in m or [M′] has only little effect on the chemical shifts of the methylenic protons. This contrasts with the situations where [m] is replaced by a halide, a phosphine, or a carbonyl group, which all induce large variations in these chemical shifts.[1c,2b]

In $^{31}P\{^1H\}$ NMR spectroscopy, the phosphorus atom bonded to [M′] can be easily distinguished by its low-field chemical shift, which is characteristic of the nature of M′ (Table II): ca. 30 ppm (when M = Pd) or 23 ppm (when M = Pt) for Co (with significant quadrupole broadening), around 42 ppm for Fe, 50 ppm for Mo, and 15 ppm for W. In the case of the clusters containing platinum, the two phosphorus atoms bonded to Pt are immediately identified by the presence of the satellites owing to coupling with ^{195}Pt.[6] The numbering of the phosphorus atoms is as follows:



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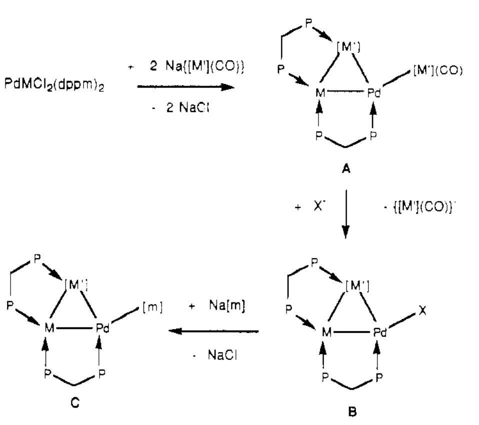
Scheme I



M = Pd, Pt; X = Cl, I; [m]⁻ = carbonylmetalate anion;
[M'] = Mo(CO)$_2$Cp, W(CO)$_2$Cp, Mn(CO)$_4$, Fe(CO)$_2$NO, Co(CO)$_3$.

In clusters **3**–**8**, replacing cobalt with iron in [M'] or [m] has little effect on the *J*(P–P) values and induces only slight variations in the chemical shifts of P(1), P(2), and P(3) (Table II). The general feature emerges that the coupling constants *J*[P(1)–P(4)] and *J*[P(1)–P(2)] ar always large and that *J*[P(2)–P(3)] is larger when M is palladium than when M is platinum. Substitution of Co, Fe, or Mn by Mo or W in [M'] induces a significant decrease in the *J*[P(1)–P(4)] values, from ca. 100–180 to ca. 30 Hz. Within this series of clusters, this is the only large effect in the ^{31}P NMR data induced by a change in the nature of the endocyclic metal M'.

Discussion

In this work, we have further extended the high-yield stepwise synthesis of tetranuclear mixed-metal clusters using carbonylmetalates as building blocks.[7] We have found that these react with dinuclear d^9–d^9 complexes of the type [PdMCl$_2$(dppm)$_2$] to afford mixed-metal clusters in which the Pd–M bond is retained, without occurrence of a redox reaction,[1-3] as also observed, e.g., with the d^9–d^9 complex [PdPtCl$_2$(μ-CO)(PPh$_3$)$_3$].[8] This contrasts with similar reactions involving, e.g., [Pd$_4$(OAc)$_4$(CO)$_4$],[9] [Pd(*o*-C$_6$H$_4$CH$_2$PPh$_2$)(μ-Cl)]$_2$,[10] or mononuclear d^8 complexes of the type [MCl$_2$L$_2$] (M = Pd, Pt; L = PR$_3$)[11] that involved redox processes. The stepwise, quantitative construction of clusters containing four different metal atoms was achieved by starting from the heterodinuclear d^9–d^9 complex [PdPtCl$_2$(dppm)$_2$] (Scheme I).[3a]

Clusters A may be formally viewed as resulting from the *regioselective* insertion (M = Pt) of the metal carbonyl fragment [M'] into a Pd–P bond of the precursor complex. In none of the reactions reported in this work did we observe a cluster core isomerization or a scrambling of the metal atoms exchanging the position of the Pd and Pt atoms (^{31}P NMR evidence), which has been observed in only one case.[3b] It is also noteworthy that insertion of a metal carbonyl fragment into the remaining Pd–P bond(s) of B does not occur upon further addition of carbonylmetalate anions.

The transformation A → B occurs immediately at room temperature and is generally quantitative, provided that the appropriate solvents have been chosen (acetone).[1c] The transformation B → C is instantaneous and quantitative at room temperature. It is more strongly solvent-dependent for X = I than for X = Cl, since, in the former case, the reverse reaction may occur, e.g., in acetone or THF. When X = Cl, the synthesis of clusters C is favored by precipitation of NaCl in THF or Et$_2$O. When X = I, however, yields are quantitative only in Et$_2$O, despite the low solubility in this medium of the species involved. In THF, reactions of clusters B (X = I) with [M]⁻ occur more readily when M = Pd than when M = Pt. This is in accord with the observation that these clusters are easier to isolate from acetone/*n*-hexane when M = Pt than when M = Pd, the reaction A + I⁻ → B + {[M'](CO)}⁻ being irreversible in the former case. This set of observations is consistent with the palladium center of the M–Pd unit being less electron-deficient when M = Pt than when M = Pd, this resulting in the general trend that the exocyclic Pd–m bond is less labile when trans to a Pd–Pd rather than a Pt–Pd bond. This "platinum effect" has been noted previously in related systems.[1c,2b,3c]

The nature of [M'] influences the optimum reaction conditions for the isolation of the tetranuclear clusters. Generally, even if the synthesis of clusters of type C is carried out in the presence of an excess carbonylmetalate, no exchange reaction is observed between the internal [M'] fragment and the incoming [m]⁻ anion. This could be due to the stabilizing effect of dppm, since related exchange reactions have been described in other cases.[12] Indeed, we have observed only one example of such an exchange: it involved the substitution of an internal Mo(CO)$_2$Cp fragment in **13a** by a Co(CO)$_3$ unit, which afforded mainly clusters **3a**. This stands in interesting contrast with previous metal-exchange reactions in which [Co] vertices are replaced by [Mo] fragments.[12]

The reactivity of [Mn(CO)$_5$]⁻, [Co(CO)$_4$]⁻, or [Fe(CO)$_3$NO]⁻ with the halogeno clusters B contrasts with the behavior of [Mo(CO)$_3$Cp]⁻ or [W(CO)$_3$Cp]⁻. It is useful at this point to remember that the reaction of these group 6 carbonylmetalates with [PdPtCl$_2$dppm)$_2$] did not lead to tetranuclear clusters A, as observed with [Mn(CO)$_5$]⁻, [Co(CO)$_4$]⁻, or [Fe(CO)$_3$NO]⁻, but instead to clusters B (with X = Cl).[1a] As unsupported Pd–Mo and Pd–W bonds are known in other molecules,[13] these observations should be taken as indication that steric hindrance could be responsible for the lability of the exocyclic Pd–metal bond. This is further substantiated by the results of the crystal structure determinations of [Pd$_2$Mn$_2$(CO)$_9$(dppm)$_2$],[2] [Pd$_2$Co$_2$(CO)$_7$(dppm)$_2$][1a,b] (type A), and [Pd$_2$MoCl(CO)$_2$Cp(dppm)$_2$][3c] (type B), which show that the metalloligand [m] = Mn(CO)$_5$, Co(CO)$_4$ or the halide X = Cl, respectively, occupy a portion of space limited by the ligands bound to [M'] and two of the phenyl rings of the Pd-bound dppm ligand. When the labilities of, e.g., **3b** and **13b** or **6b** and [PdPtMo$_2$Cp$_2$(CO)$_5$(dppm)$_2$][3c] are compared, the size of this "pocket" appears to decrease in the order [M'] = Co(CO)$_3$ $\gg$ Mo(CO)$_2$Cp. If one considers that a Cp ligand is sterically equivalent to three carbonyls,[14] the lability observed for the Pd–[m] bond in clusters of type C principally reflects, at [M'] constant, the steric hindrance of the metalloligand [m], which both increase in the sequence [m] = Co(CO)$_4$ $\leq$ Fe(CO)$_3$NO $\ll$ Mn(CO)$_5$ $\ll$ Mo(CO)$_3$Cp $\approx$ W(CO)$_3$Cp.

Whereas CO-induced heterolytic cleavage of the exocyclic Pd–Co bond is complete in **13b**, it is only partial for the exocyclic Pd–Mo bond in its structural isomer **6b**. Combining this and other information available for [PdMCo$_2$(CO)$_7$(dppm)$_2$] (**3**)[1c] and [PdMMo$_2$Cp$_2$(CO)$_5$(dppm)$_2$][3c] allows one to evaluate the relative weight of the two main parameters that control the chemistry of the metalloligated clusters belonging to this family: the steric bulk of the exocyclic metalloligated fragment and that of the endocyclic one. Thus, it appears that the reactivity of the exocyclic metal–metal bond toward CO in THF decreases as a function of the tetranuclear core in the sequence PdPtMo$_2$ $\approx$ Pd$_2$Mo$_2$ $\approx$ PdPtMoCo (**13b**) $\approx$ Pd$_2$MoCo (**13a**) > PdPtCoMo (**6b**) > Pd$_2$CoMo

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(**6a**) > $PdPtCo_2$ (**3b**) ≈ Pd_2Co_2 (**3a**).

Experimental Section

All reactions were carried out under dry dinitrogen in Schlenk-type flasks. Toluene, hexane, and pentane were dried over sodium and distilled before use. Other general techniques and reagents were used as previously described.[1,2] The following clusters were synthesized according to previous work: $[PdMCoX(CO)_3(dppm)_2]$ (M = Pd, Pt; X = Cl, I),[1b,c] $[Pd_2FeI(CO)_2(NO)(dppm)_2]$,[2b] $[Pd_2MnCl(CO)_4(dppm)_2]$,[2b] $[PdMMoCpCl(CO)_2(dppm)_2]$ (M = Pd, Pt), and $[Pd_2WCpCl(CO)_2(dppm)_2]$.[3c] Solutions of $Na[Mn(CO)_5]$ and $Na[Co(CO)_4]$ were prepared by Na/Hg reduction of THF solutions of $[Mn_2(CO)_{10}]$[15] and $[Co_2(CO)_8]$,[16] respectively. $K[Fe(CO)_3NO]$ was prepared by the reaction of $[Fe(CO)_5]$ with KNO_2.[17] The synthesis of $Na[Mo(CO)_3Cp]\cdot 2DME$ (Cp = η-C_5H_5) and $Na[W(CO)_3Cp]\cdot 2DME$ have been previously described.[11] Infrared spectra were recorded in the region 4000–400 cm^{-1} on a Perkin-Elmer 398 spectrophotometer or on a Bruker IFS66 FTIR spectrophotometer. NMR spectra were recorded on a FT-Bruker WP 200 SY instrument at 200.13 MHz (^1H) or 81.02 MHz (^{31}P) using solvent resonances as internal standards and referenced to $SiMe_4$ (^1H) or 85% H_3PO_4 (^{31}P). Elemental analyses were performed by the Service Central d'Analyses du CNRS.

Synthesis of $[Pd_2Co_2(CO)_7(dppm)_2]$ (3a). A solution of $Na[Co(CO)_4]$ in THF (0.05 M, 2 mL) was added to a solution of $[Pd_2CoCl(CO)_3(dppm)_2]$ (**1a**) (0.100 g, 0.09 mmol) in THF (20 mL). The reaction mixture immediately turned from red-brown to deep green. The solvent was removed in vacuo, and the green residue was extracted with toluene. The resulting solution mixture was filtered, and addition of *n*-hexane afforded **3a** (0.100 g, 86% based on Pd), which was identified (IR and NMR spectroscopy) by comparison with an authentic sample.[1]

Synthesis of $[Pd_2CoFe(CO)_6(NO)(dppm)_2]$ (4a). A solution of $K[Fe(CO)_3NO]$ (0.030 g, 0.14 mmol) in Et_2O (10 mL) was added to a stirred suspension of $[Pd_2CoCl(CO)_3(dppm)_2]$ (**1a**) (0.140 g, 0.12 mmol) in Et_2O (150 mL). The color immediately changed from red-brown to deep green. Et_2O was removed under vacuum, and the resulting green residue was extracted with toluene (100 mL). The solution was filtered, and addition of *n*-hexane induced the precipitation of **4a** as a black-green powder (0.112 g, 72% based on Pd; mp 176 °C dec). Anal. Calcd for $C_{56}H_{44}CoFeNO_7P_4Pd_2$ (M_r = 1294.45): C, 51.96; H, 3.43; N, 1.08. Found: C, 51.51; H, 3.46; N, 1.47. ^1H NMR (toluene-d_8): δ 7.84–6.92 (40 H, m, Ph), 4.55 (2 H, dt, $^2J(P-H)$ = 8.6 Hz, $^4J(P-H)$ = 3 Hz, CH_2), 3.89 (2 H, t, $^2J(P-H)$ = 9.7 Hz, CH_2).

Synthesis of $[PdPtCoFe(CO)_6(NO)(dppm)_2]$ (4b). Solid $K[Fe(CO)_3NO]$ (0.027 g, 0.13 mmol) was added to a red suspension of $[PdPtCoI(CO)_3(dppm)_2]$ (**2b**) (0.121 g, 0.090 mmol) in Et_2O (100 mL). After being stirred for 4 h at room temperature, the green solution was concentrated under vacuum (to ca. 10 mL), affording a green precipitate, which was filtered off and dissolved in toluene (80 mL). The green solution was filtered, and addition of pentane (40 mL) gave a green powder of **4b** (0.065 g, 0.047 mmol, 52% based on Pt). Anal. Calcd for $C_{56}H_{44}CoFeNO_7P_4PdPt$ (M_r = 1383.14): C, 48.59; H, 3.21; N, 1.01. Found: C, 48.94; H, 3.38; N, 0.94.

Synthesis of $[Pd_2CoMn(CO)_8(dppm)_2]$ (5a). A solution of $Na[Mn(CO)_5]$ in THF (0.10 M, 0.4 mL) was added to a suspension of $[Pd_2CoI(CO)_3(dppm)_2]$ (**2a**) (0.050 g, 0.040 mmol) in Et_2O (50 mL). The color of the reaction mixture immediately changed from red-brown to deep green. *n*-Hexane (50 mL) was then added, inducing precipitation of a green solid. This was collected by filtration, dried, and redissolved in toluene (40 mL), affording a deep green solution, which was then filtered. The volume of the solution was reduced to ca. 15 mL by evaporation in vacuo. Addition of *n*-hexane afforded dark green microcrystals of **5a** (0.034 g, 64% based on Pd; mp 180 °C dec). Anal. Calcd for $C_{58}H_{44}CoMnO_8P_4Pd_2$ (M_r = 1319.56): C, 52.79; H, 3.36. Found: C, 52.46; H, 3.60. ^1H NMR (toluene-d_8): δ 7.78–6.84 (40 H, m, Ph), 4.62 (2 H, t, $^2J(P-H)$ = 7.2 Hz, CH_2), 3.94 (2 H, t, $^2J(P-H)$ = 8.7 Hz, CH_2).

Alternatively, $[Pd_2CoCl(CO)_3(dppm)_2]$ was reacted with the stoichiometric amount of $Na[Mn(CO)_5]$, following the procedure described above, in THF instead of Et_2O. Similar yields of **5a** were obtained.

Synthesis of $[PdPtCoMn(CO)_8(dppm)_2]$ (5b). A filtered solution of $Na[Mn(CO)_5]$ (0.1 M) in THF (2 mL) was added to a suspension of **2b** (0.128 g, 0.096 mmol) in toluene (40 mL)/Et_2O (40 mL). The color of the reaction mixture changed from red to green after 0.25 h of stirring at room temperature. The green solution was filtered through a silica-padded filter funnel (medium porosity) and evaporated to dryness in vacuo. Extraction with toluene (40 mL) gave a green solution. Filtration and addition of pentane (75 mL) afforded a green powder of **5b** (0.092 g, 68% based on Pt). Anal. Calcd for $C_{58}H_{44}CoMnO_8P_4PdPt$ (M_r = 1408.24): C, 49.47; H, 3.15; Co, 4.18; Mn 3.90; P, 8.80. Found: C, 49.14; H, 3.34; Co, 3.63; Mn, 2.98; P, 7.30. ^1H NMR (CD_2Cl_2): δ 7.54–6.82 (40 H, m, Ph), 4.96 (2 H, m, CH_2), 4.45 (2 H, m, CH_2).

Preparation of $[Pd_2CoMoCp(CO)_6(dppm)_2]$ (6a). Upon addition of a solution of $Na[Mo(CO)_3Cp]\cdot 2DME$ (0.068 g, 0.152 mmol) in THF (10 mL) to a red solution of **1a** (0.171 g, 0.147 mmol) in THF (20 mL), the reaction mixture became brown-green. THF was removed, the residue was extracted with toluene (20 mL), and the extract was filtered through a Celite-padded filter funnel. The solution studies were undertaken immediately because of the rapid decomposition of **6a** at room temperature. The ^{31}P NMR and IR data of the solution revealed a quantitative conversion to **6a**.

IR Monitoring of the Reaction of 6a with CO in THF. A solution of **6a** turned brown upon standing under a CO atmosphere. IR analysis of the mixture revealed, together with absorptions due to **6a**, new bands at 1899 (sh) and 1785 (m) cm^{-1}, indicative of the presence of $[Mo(CO)_3Cp]^-$, and a very weak band at 2073 cm^{-1}, characteristic of the cation $[Pd_2Co(CO)_4(dppm)_2]^+$.[1c]

Preparation of $[PdPtCoMoCp(CO)_6(dppm)_2]$ (6b). Upon addition of a solution of $Na[Mo(CO)_3Cp]\cdot 2DME$ (0.052 g, 0.116 mmol) in THF (5 mL) to a red solution of **1b** (0.130 g, 0.104 mmol) in THF (10 mL), the reaction mixture became deep green. THF was removed, the residue was extracted with toluene (20 mL), and the extract was filtered through a Celite-padded filter funnel. The solution studies were undertaken immediately because of the rapid decomposition of **6b** at room temperature. The ^{31}P NMR and ^1H NMR data of the solution revealed a quantitative conversion to **6b**. ^1H NMR (toluene-d_8): δ 7.67–6.59 (40 H, m, Ph), 4.87 (5 H, s, Cp), 4.78 (2 H, m, CH_2), 3.89 (2 H, t, $^2J(P-H)$ = 9.8 Hz, $J(Pt-H)$ = 36 Hz, CH_2).

When a green solution of **6b** in toluene was stirred for 24 h at room temperature, its color turned to red, and a ^{31}P NMR analysis of the products in a mixture of CH_2Cl_2 and $CDCl_3$ revealed the presence of only **1b**.

IR Monitoring of the Reaction of 6b with CO and PPh_3 in THF. A green solution of **6b** turned green-brown upon standing under a CO atmosphere. IR analysis of the mixture revealed, together with absorptions due to **6b**, new bands at 1898 (vs) and 1782 (s) cm^{-1}, indicative of the presence of $[Mo(CO)_3Cp]^-$, and a weak band at 2066, characteristic of $[PdPtCo(CO)_4(dppm)_2]^+$. Note that addition of PPh_3 to the mixture caused an immediate color change to light red and that the IR analysis (2008 (m), 1898 (vs), 1886 (m), 1782 (vs) cm^{-1}) of the red solution showed that complete dissociation into $[PdPtCo(CO)_3(PPh_3)(dppm)_2][Mo(CO)_3Cp]$ had occurred.[1c] From these data, the ratio $[PdPtCo(CO)_4(dppm)_2][Mo(CO)_3Cp]$:**6b** was estimated to be 1:6.

Synthesis of $[Pd_2FeCo(CO)_6(NO)(dppm)_2]$ (8). Solid $Na[Co(CO)_4]$ (0.035 g, 0.180 mmol) was added to a suspension of **7** (0.210 g, 0.170 mmol) in Et_2O (60 mL). The color of the reaction mixture immediately turned from red-brown to deep green. After the mixture was stirred for 1 h, *n*-hexane was added and the resulting solid was collected by filtration and redissolved in toluene (150 mL). The solution was filtered to remove insoluble NaI and its volume reduced to ca. 50 mL. Recrystallization from *n*-hexane afforded a dark green powder of **8** (0.2025 g, 94% based on Pd). Anal. Calcd for $C_{56}H_{44}CoFeNO_7P_4Pd_2$ (M_r = 1294.45): C, 51.96; H, 3.43; N, 1.08; Co, 4.55; Fe, 4.31; Pd, 16.44. Found: C, 49.51; H, 3.46; N, 0.82; Co, 4.72; Fe, 3.46; Pd, 15.78. ^1H NMR (toluene-d_8): δ 7.86–6.86 (40 H, m, Ph), 4.49 (2 H, dt, $^2J(P-H)$ = 8.0 Hz, $^4J(P-H)$ = 3 Hz, CH_2), 3.80 (2 H, t, $^2J(P-H)$ = 9.5 Hz, CH_2).

Reaction of 8 with an Excess of $[Co(CO)_4]^-$. A suspension of **8** (0.05 g, 0.04 mmol) in Et_2O (5 mL) was stirred with $Na[Co(CO)_4]$ (10-fold excess) for 12 h. The solvent was removed under vacuum. Extraction of the residue with toluene quantitatively afforded unchanged **8**.

Synthesis of $[Pd_2Mn_2(CO)_9(dppm)_2]$ (10). A filtered solution of $Na[Mn(CO)_5]$ in THF (0.10 M, 0.5 mL) was added to a solution of **9** (0.054 g, 0.046 mmol) in THF (5 mL). The color of the reaction mixture changed immediately from green to violet, and the solvent was removed under vacuum after 0.5 h. The residue was then extracted with toluene. The solution was filtered, and addition of *n*-hexane afforded **10** as dark violet microcrystals (0.05 g, 82% based on Pd). The product was identified (IR and NMR spectroscopy) by comparison with an authentic sample.[2]

Reaction of $[Pd_2MoCl(CO)_2Cp(dppm)_2]$ with $[Mo(CO)_3Cp]^-$. A suspension of $Na[Mo(CO)_3Cp]\cdot 2DME$ (0.021 g, 0.047 mmol) in Et_2O (20 mL) was added to a suspension of $[Pd_2MoCl(CO)_2Cp(dppm)_2]$ (0.046 g, 0.037 mmol) in Et_2O (25 mL) at 0 °C. After 0.25 h, the color of the reaction mixture turned from yellow-brown to blue-green. Stirring was maintained for 3 h at 0 °C, and the solution was filtered to remove some insoluble brown material. A sample of the blue-green solution was evaporated to dryness, and an attempt was made to record the IR spec-

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trum of the solid. During preparation of the KBr pellet, the green solid turned brown and the IR spectrum showed bands of $[Mo_2(CO)_6Cp_2]$ and of $[Pd_2MoBr(CO)_2Cp(dppm)_2]$. When another evaporated sample of the blue-green solution was redissolved in THF, it turned immediately brown. The blue-green Et_2O solution was kept at -20 °C. After 48 h, a yellow-brown solid precipitated (identified as $[Pd_2MoCl(CO)_2Cp(dppm)_2]$) and the supernatant contained $[Mo_2(CO)_6Cp_2]$. When this reaction was carried out in THF instead of Et_2O, it never led to a green solution but instead to a brown solution. However, using a slightly different workup allows isolation of the desired cluster $[Pd_2Mo_2Cp_2(CO)_5(dppm)_2]$.[3c]

Synthesis of $[Pd_2MoCoCp(CO)_6(dppm)_2]$ (13a). A solution of Na$[Co(CO)_4]$ (0.7 mL of a 0.1 M solution in THF) was added to a solution of **11a** (0.086 g, 0.070 mmol) in THF (5 mL). Upon addition, the solution turned from a dark honey color to red violet. The solvent was removed, and the solid was extracted with toluene (15 mL), affording a brown-violet solution. Dark brown crystals of **13a** were obtained by cooling at -20 °C (0.063 g, 0.046 mmol, 66% based on Pd). Anal. Calcd for $C_{61}H_{49}CoMoO_6P_4Pd_2$ (M_r = 1369.7): C, 53.49; H, 3.61. Found: C, 52.91; H, 3.96. ^{1}H NMR (toluene-d_8): δ 7.66-6.55 (40 H, m, Ph), 4.77 (5 H, s, Cp), 4.21 (2 H, t, ^2J(P-H) = 7.5 Hz, CH_2), 3.57 (2 H, t, ^2J(P-H) = 9.3 Hz, CH_2).

Metal-Exchange Reaction: Conversion of 13a into 3a. A toluene solution of cluster **13a**, prepared as described above from **11a** (0.056 g, 0.045 mmol) and K$[Co(CO)_4]$ (0.019 g, 0.09 mmol), was stirred for 3 days, during which time the color of the mixture changed from the original brown-violet to deep green and an insoluble dark material formed. Filtration through Celite and recrystallization from THF/*n*-hexane afforded a dark green powder of **3a** (0.025 g, 0.019 mmol, 42% yield based on Pd, 84% based on Co).

Synthesis of $[PdPtMoCoCp(CO)_6(dppm)_2]$ (13b). A brown mixture of **11b** (0.133 g, 0.100 mmol) and Na$[Co(CO)_4]$ (1 mL of a 0.1 M solution in THF) in THF (30 mL) was stirred for 1 day, after which time the solvent was removed. Extraction of the solid with toluene (20 mL) afforded a brown-violet solution. Dark brown crystals of **13b** were obtained by cooling at -20 °C (0.1015 g, 0.072 mmol, 72% based on Pt). Anal. Calcd for $C_{61}H_{49}CoMoO_6P_4PdPt$ (M_r = 1458.3): C, 50.24; H, 3.39. Found: C, 50.02; H, 3.64. ^{1}H NMR (toluene-d_8): δ 7.72-6.61 (40 H, m, Ph), 4.94 (5 H, d, J(P-H) = 1.5 Hz, Cp), 4.61 (2 H, t, ^2J(P-H) = 8.6 Hz, J(Pt-H) = 63 Hz, CH_2), 3.82 (2 H, t, ^2J(P-H) = 10.1 Hz, J(Pt-H) = 38.4 Hz, CH_2).

Synthesis of $[Pd_2WCo(CO)_6Cp(dppm)_2]$ (14). Solid Na$[Co(CO)_4]$ (0.011 g, 0.060 mmol) was added to a suspension of $[Pd_2WCl(CO)_2Cp(dppm)_2]$ (**12**) (0.065 g, 0.049 mmol) in Et_2O (20 mL) at -78 °C. The temperature was raised to ambient, and the color of the reaction mixture turned from yellow-brown to deep red. *n*-Hexane was added, and the resulting solid, which was collected by filtration, was separated from NaCl and excess Na$[Co(CO)_4]$ by dissolution in toluene (50 mL). The resulting violet solution was concentrated to ca. 20 mL, and an equal volume of *n*-hexane was added. This afforded **14** as dark violet microcrystals (0.065 g, 89% based on Pd). Anal. Calcd for $C_{61}H_{49}CoO_6P_4Pd_2W$ (M_r = 1457.54): C, 50.27; H, 3.39. Found: C, 50.41; H, 3.45. ^{1}H NMR (toluene-d_8): δ 7.28-6.81 (40 H, m, Ph), 5.05 (5 H, s, Cp), 4.59 (2 H, t, ^2J(P-H) = 8.7 Hz, CH_2), 4.13 (2 H, t, ^2J(P-H) = 9.7 Hz, CH_2).

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Preparation, Characterization, and Catalytic Activity of a New Solid Acid Catalyst System

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A series of novel, solid, strong acids have been prepared by the reaction of inorganic oxides with Al_2Cl_6. The objective was to create a solid acid with tetrahedral aluminum centers, which are expected to be stronger Lewis acids than octahedral aluminum centers. Investigations of the acid sites of these solids by the infrared spectroscopy of adsorbed pyridine, calorimetric titrations, and solid-state nuclear magnetic resonance confirm that new strong solid acids have been prepared. The systems exhibit high catalytic activity and selectivity for acid-catalyzed cracking reactions under very mild conditions where present commercial catalysts do not react.

Introduction

Because of the reported advantages of solid acid catalysts, recent research has focused on the preparation and characterization of stronger solid acids.[1-3] These materials exhibit extremely high catalytic activity for reactions such as isomerization, cracking, hydrocracking, dehydration, alkylation, acylation, conversion of methanol to gasoline, etc.[1] Many attempts have been made to use metal halides as homogeneous acid catalysts, and one of the most frequently studied inorganic Lewis acids is aluminum chloride. Aluminum chloride was tested commercially in cracking but was abandoned because of technical difficulties such as corrosion, separation of phases, difficulty in the recovery of the catalyst, and the formation of high molecular weight hydrocarbons.[3,4] As a result, recent research has focused on the anchoring of homogeneous acid catalysts onto inorganic oxides for use as solid acid catalysts.[1-6]

Many patents have been issued for the treatment of inorganic oxides with aluminum chloride.[7-14] The most common method of treating hydroxylated inorganic oxides with aluminum chloride is by vapor deposition.[2,7-13] The vapors of aluminum chloride are passed through the inorganic oxide by using a carrier gas such as helium,[6,8,9,11,13] or aluminum chloride is sublimed from a mixture of the inorganic oxide and aluminum chloride.[10,13] The reaction of aluminum chloride and the inorganic oxide in a solvent has been employed as an alternative to vapor deposition.[7] Past attempts[7] of this reaction have employed solvents other than CCl_4, for example, chloroform ($CHCl_3$), methylene chloride (CH_2Cl_2), ethylene dichloride ($ClCH_2CH_2Cl$), and saturated hydrocarbons. We report that employing CCl_4 with the procedure reported herein

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