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FULL PAPER

An entry to half-sandwich complexes of first row transition metals (Ni, Co, Mn) containing the Kläui tripodal ligand, L_{OMe}: synthesis and crystal structures of oligomeric, $[L_{OMe}M(\mu\text{-}X)(L)]_n$ (n = 2, 4), and monomeric complexes, $L_{OMe}M(L_2)(X)$

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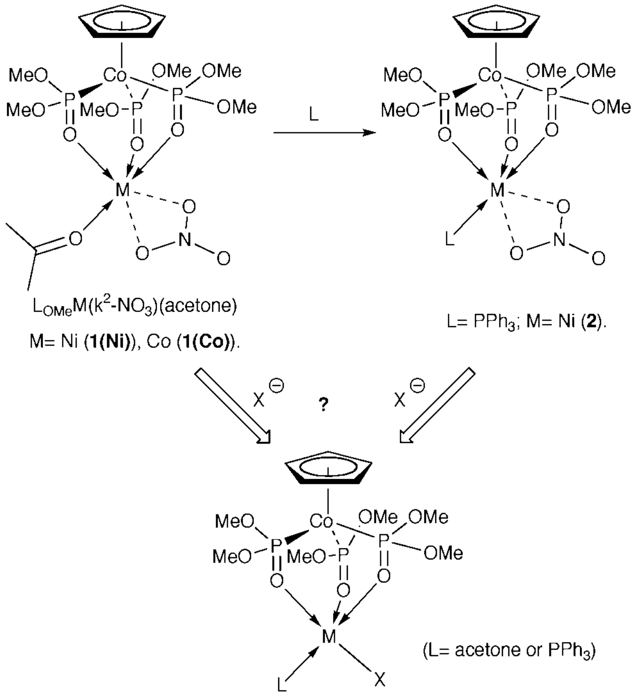
A series of half-sandwich complexes of Ni, Co and Mn containing the Kläui tripodal ligand L_{OMe} [κ^3-(η^5-C_5H_5)Co{P(=O)($OCH_3)_2$}$_3$] are prepared by reaction of the labile precursors, $L_{OMe}M(L)(\kappa^n\text{-}NO_3)$ [M = Ni, Co; L = acetone (**1**, n = 2), PPh_3 (**2**, n = 2), κ^2-bipy (**8**, n = 1), κ^2-tmeda (**9**, n = 1)] and $[L_{OMe}Mn(py)(\mu\text{-}NO_3)]_2$ (**15**), with anionic N- and O-nucleophiles. Oligomeric complexes are formed from complexes **1**, **2**, and **15** *via* elimination of the κ^1-ligands (L). Reactions with NaN_3 and sodium aryloxide (NaOAr) afford the tetrameric μ_3-azido complexes, $[L_{OMe}M(\mu_3\text{-}N_3)]_4$ (**3**), and the dimeric μ-aryloxo complexes, $[L_{OMe}M(\mu\text{-}OAr)(X)]_2$ (**5**, **6**: Ar = 2,6-Me_2-C_6H_3, 2,4,6-Me_3-C_6H_2, 2- and 4-NO_2-C_6H_4, C_6F_5; X = none, ROH), respectively, but the sandwich complexes $(L_{OMe})_2M$ result from reactions with other O-nucleophiles such as NaOH, NaOR, and NaOAr [Ar = C_6H_5, 4-MeC_6H_4, 2,6-X_2-C_6H_3 (X = F, Cl)]. Mononuclear complexes $L_{OMe}M(\kappa^2\text{-}L)(\kappa^1\text{-}NO_3)$ **8** and **9** are obtained by treatment of **1** or **2** with bidentate ligands and further converted to $L_{OMe}M(\kappa^2\text{-}L)$-X-type azido (**10**, **11**), halo (**12**), aryloxo (**13**) and MeCN-coordinated cationic complexes (**14**).

Introduction

The Kläui ligands, L_{OR} [(η^5-C_5H_5)Co{P(=O)(OR)$_2$}$_3$],[1] are unique tripodal O_3-ligands, and their coordination chemistry has been studied extensively as compared with other 6e-donors such as N_3-donors (*e.g.* hydrotrispyrazolylborates (Tp^R)[2] and triazacycloalkanes[3]) and cyclopentadienyl ligands (η^5-C_5R_5) (R = hydrocarbyl).

In sharp contrast to the well-developed chemistry of $L_{OR}M(X)_n$-type half-sandwich complexes of main group elements and second and third row transition metals, the corresponding derivative chemistry of first row transition metal complexes has been extremely limited.[1] Attempted synthesis is frequently associated with formation of undesirable, kinetically inert full-sandwich complexes, $(L_{OR})_2M$, and few examples of $L_{OR}M(X)_n$-type half-sandwich complexes have been reported so far.[4] We are currently studying the synthesis of first row transition metal half-sandwich complexes, L_{OR}-M–X, with a transformable functional group (X) and, in our previous paper, we reported the selective synthesis of labile complexes **1**, $L_{OMe}M(\kappa^2\text{-}NO_3)$(acetone) (M = Ni, Co), by overcoming the above-mentioned problem, *i.e.* formation of $(L_{OMe})_2M$ (Scheme 1).[5] The κ^2-coordination of the nitrato ligand prevents interaction with a second equivalent of L_{OR}^- to result in selective formation of 1 : 1 adducts. In the previous paper we also reported substitution of the labile acetone ligand by 2e-donors to lead to $L_{OMe}M(L)(NO_3)$-type complexes such as **2** and herein we disclose results of functionalization of the labile acetone (**1**) and PPh_3 complexes (**2**) *via* replacement of the κ^2-nitrate ligand by anionic ligands. Formation of oligomeric products mainly results from dissociation of the labile ligands (acetone and PPh_3), and mononuclear complexes are obtained upon introduction of bidentate ligands in place of L.



Scheme 1

Results and discussion

Reaction of $L_{OMe}M(\kappa^2\text{-}NO_3)(L)$ (L = acetone (1), PPh_3 (2)) with anionic ligands

We examined reactions of complexes **1** and **2** with a variety of N- and O-nucleophiles. The results were dependent on

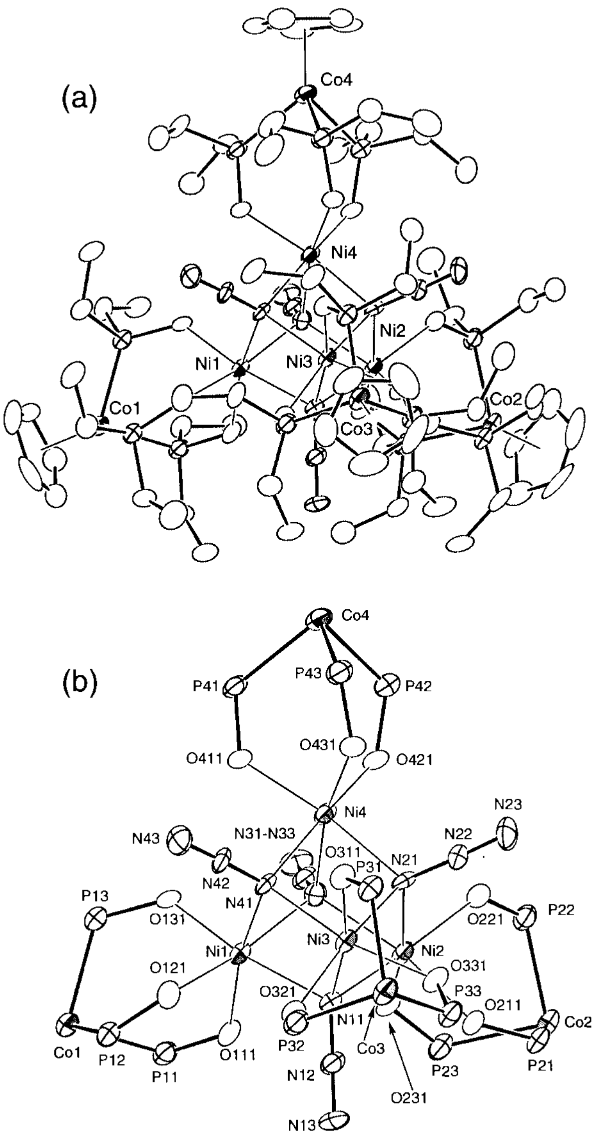
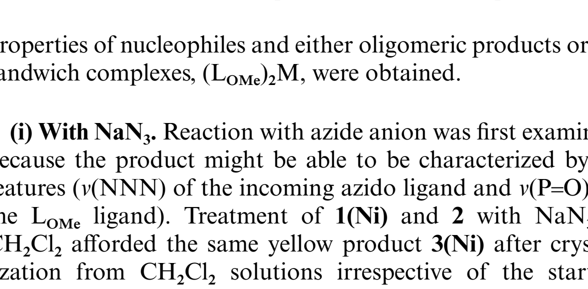


Fig. 1 Molecular structures of **3(Ni)** drawn at the 30% probability level. (a) An overview. (b) An expanded view of the core part.

properties of nucleophiles and either oligomeric products or the sandwich complexes, $(L_{OMe})_2M$, were obtained.

(i) With NaN$_3$. Reaction with azide anion was first examined, because the product might be able to be characterized by IR features (ν(NNN) of the incoming azido ligand and ν(P=O) for the L_{OMe} ligand). Treatment of **1(Ni)** and **2** with NaN_3 in CH_2Cl_2 afforded the same yellow product **3(Ni)** after crystallization from CH_2Cl_2 solutions irrespective of the starting materials, and similar reaction of **1(Co)** gave pink crystals (**3(Co)**) (eqn. (1)). The IR spectra of **3** revealed the presence of



(1)

N_3 and L_{OMe} ligands but no evidence for the acetone and PPh_3 ligand present in the starting complexes **1** and **2**, respectively, was obtained. The molecular structure of the Ni complex **3(Ni)** was determined by X-ray crystallography. An ORTEP[14] view is shown in Fig. 1 and averaged structural parameters are summarized in Table 1. As a result, the product **3(Ni)** turned out to be a cubane-like tetrameric complex without acetone or PPh_3 ligand in accord with the IR data. The cobalt complex **3(Co)** also adopted a similar structure, although the structure could not be refined satisfactorily due to the low quality of the crystals.[6]

Table 1 Selected structural parameters for **3(Ni)**[a]

Ni–N	2.169–2.218(9)	Co–P	2.147–2.176(4)
Ni–O	2.025–2.048(9)	Co–Cp	2.02–2.11(2)
NiN–N$_2$	1.21(1)	P–O	1.478–1.512(9)
NiN$_2$–N	1.13–1.15(2)	C–C	1.31–1.47(3)
N–Ni–N	79.8–81.5(4)	N–Ni–O	86.6–89.5(4)
N–N–N	178–179(1)		100.3–102.5(4)
Ni–N–Ni	97.2–99.6(4)		166.9–169.8(4)
Ni–N–N	117.3–119.7(8)	O–Ni–O	89.4–92.3(3)
		P–Co–P	89.5–91.4(2)

[a] Bond lengths (Å) and bond angles (°), averaged values.

Triangular faces of the Ni_4 tetrahedron with essentially the same edge lengths [Ni···Ni: 3.247(2)–3.276(3) Å] are capped by μ_3-azido ligands in a symmetrical manner as indicated by the Ni–N distances in the narrow range [2.169–2.218(9) Å]. When the structural parameters are compared with those of the mononuclear η^1-azido complex **10** (see below), the Ni–N distances are slightly longer than in **10** (2.091(4) Å) and notable desymmetrization of the N–N lengths is observed. The difference can be interpreted in terms of the resonance structure **A**, which is in contrast to the allene-like resonance structure **B** for the mononuclear complex **10** (Chart 1).

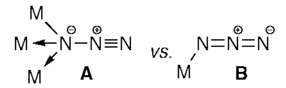


Chart 1

A related cubane-like complex, $Ni_4(N_3)_4(dbm)_4(EtOH)_4$ (dbmH = dibenzoylmethane), was already reported by Christou *et al.* and its structural parameters for the core part were very similar to those of **3(Ni)**.[7]

The reaction should initially form a labile **B**-type monomeric intermediate, $L_{OMe}M(N_3)(L)$, which would be converted to **3** through displacement of L by the sp^2-hybridized α-nitrogen atom of the coordinated azido ligand. In the previous paper, we reported the labile character of **1** and dissociation equilibrium of the PPh_3 ligand in **2**.[5] The formation of the tetrameric structure should be a result of thermodynamic stability of the cubane-like structure.

(ii) With oxygen nucleophiles. Reaction of **1** or **2** with $^-$OH and $^-$OR anions[8] was studied intensively but the disproportionation products, $(L_{OMe})_2M$ **4**,[9] were usually isolated and no evidence for formation of the desired hydroxo and alkoxo complexes was obtained. The octahedral structure of **4(Ni)** with the Ni–O lengths of 2.050–2.064(3) Å and the O–Ni–O angles of 89.4–90.7(1)° was determined by X-ray crystallography.

In contrast to the reactions of the above-mentioned oxygen nucleophiles, reaction of **1** or **2** with aryloxides afforded four types of products **4**–**7** depending on the properties of the nucleophiles. The results are summarized in Scheme 2.

Dinuclear complexes were obtained from bulky (**a**,**b**) or less basic aryloxides (**c**–**e**) but the reactions of **1(Ni,Co)** and **2** with other aryloxides such as $NaOC_6H_4$-4-Me (pK_a 10.26), $NaOC_6H_5$ (9.99), $NaOC_6H_4$-4-F (9.81), $NaOC_6H_4$-4-Cl (9.37), $NaOC_6H_3$-2,6-F_2 (not available), and $NaOC_6H_3$-2,6-Cl_2 (6.78) (values in parentheses are pK_a values for the corresponding ArOH)[10] afforded **4(Ni,Co)**. Reactions of $NaOC_6H_3$-2,6-F_2 and $NaOC_6H_3$-2,6-Cl_2, which were less basic than $NaOC_6H_4$-2 and 4-NO_2 (**c** and **d**) and similar to $NaOC_6F_5$ (**e**) with respect to the

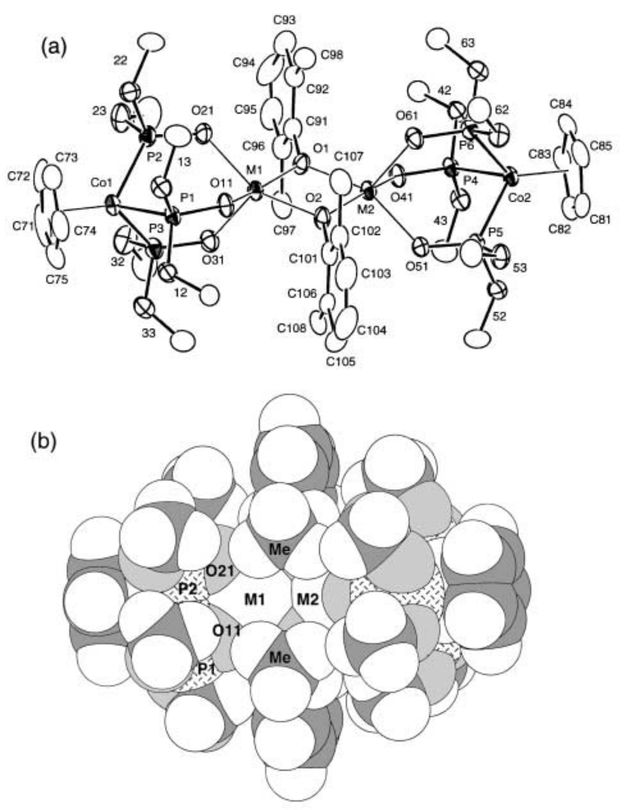
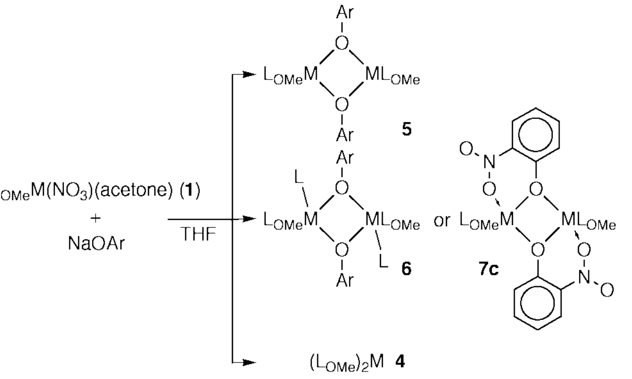


Fig. 2 Molecular structure of **5b(Co)** drawn at the 30% probability level (M1 = Co3, M2 = Co4). (a) An overview. (b) A bottom view of a space-filling model. Labels without atom names are for the methoxy groups.



Substituents of OAr	pK_a [a]	M Ni	 Co
2,4,6-Me_3 (**a**)	10.88	**5a(Ni)** (35%)	**5a(Co)** (42%)
2,6-Me_2 (**b**)	10.59	**5b(Ni)** (73%)	**5b(Co)** (51%)
2-NO_2 (**c**)	7.23	**7c(Ni)** (67%)	**7c(Co)** (64%)
4-NO_2 (**d**)	7.15	**6d(Ni)** (65%; L= MeOH)	[b]
F_5 (**e**)	5.3	**5e(Ni)** (43%), **6e(Ni)** (L= H_2O) [c]	**5e(Co)** (53%)

[a] pK_a values for ArOH. [b] No pure product was obtained. [c] See text.

Scheme 2

bulkiness, did not afford dinuclear complexes but the sandwich complex **4** despite many attempts under various reaction conditions.

Molecular structures of **5b(Ni)**, **5b(Co)**, **6d(Ni)**, **6e(Ni)** and **7c(Ni)** determined by X-ray crystallography are divided into two classes: five-coordinate structure **5** and six-coordinate structures **6** and **7**. ORTEP views of **5b(Ni)**, **6d(Ni)**, **6e(Ni)** and **7c(Ni)** are shown in Figs. 2–4.[11]

Selected structural parameters for the six-coordinate complexes **6d,e(Ni)** and **7c(Ni)** are listed in Table 2. In addition to the κ^3-coordinated L_{OMe} ligand and the bridging OAr ligand, extra-coordination of solvent molecules (MeOH or H_2O) or chelation of the *o*-nitro group constitutes six-coordinate structures. Coordination environment of the Ni centers can be described as virtually regular octahedrons, because the inter-ligand angles except the O1–Ni–O2 angle are close to the right angle. The Ni–O distances are divided into two categories: one for neutral ligands (ROH and NO_2 substituent) longer than 2.1 Å and the other for anionic ligands (O=P and OAr) shorter than 2.1 Å. Despite the chelating structure, structural features of the chelating complex **7c(Ni)** are similar to those of the non-chelating complexes **6d,e(Ni)** and no notable differences were found.

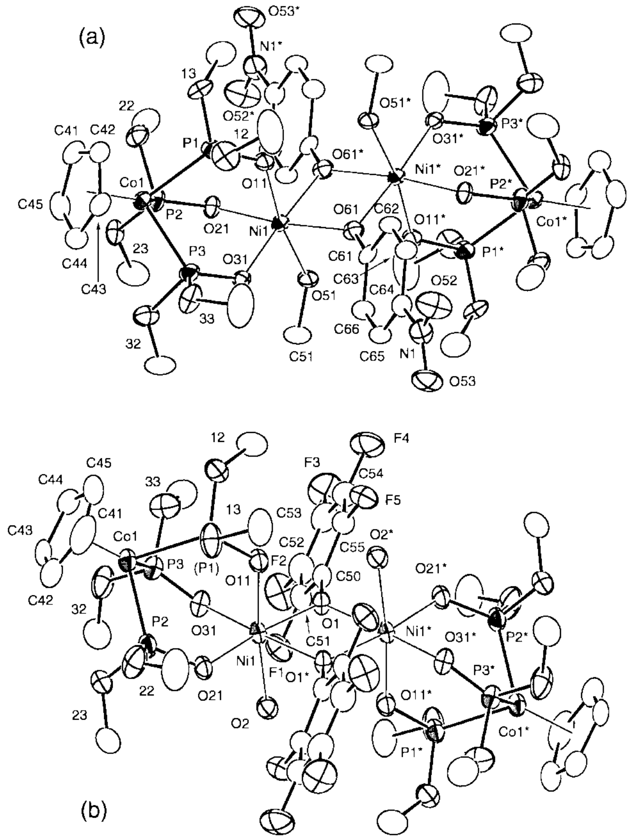


Fig. 3 Molecular structures of (a) **6d(Ni)** and (b) **6e(Ni)** drawn at the 30% probability level. Details as in Fig. 2.

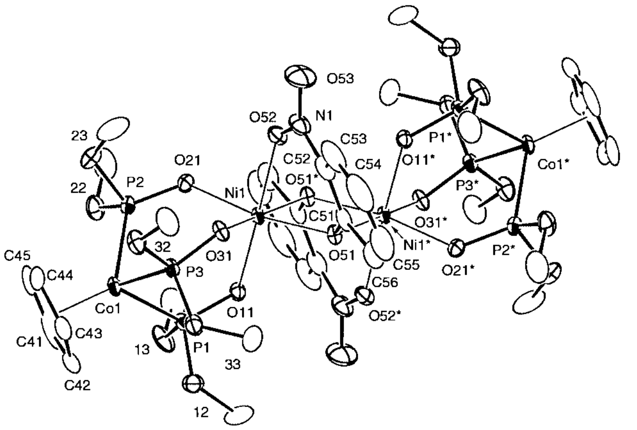


Fig. 4 Molecular structure of **7c(Ni)** drawn at the 30% probability level. Details as in Fig. 2.

When the 2,6-dimethyl derivative, a bulky aryloxide, was used, five-coordinate complexes **5b(Ni,Co)** were obtained instead of six-coordinate complexes. The 2,4,6-trimethyl derivatives **5a(Ni,Co)** were also assigned to the five-coordinate dinuclear structures on the basis of the very similar features of

Table 2 Selected structural parameters for $[L_{OMe}M(OAr)(X)]_2$, **6d(Ni)**, **6e(Ni)**, **7c(Ni)** and **7c(Mn)**[a]

Complex	**6d(Ni)**[b]		**6e(Ni)**	**7c(Ni)**	**7c(Mn)**[b]	
Ar (X)	*p*-NO_2-C_6H_4 (MeOH)		C_6F_5 (H_2O)	*o*-NO_2-C_6H_4 (NO_2)[c]	*o*-NO_2-C_6H_4 (NO_2)[c]	
Co–P	2.154–2.165(3)	2.154–2.165(3)	2.159–2.165(2)	2.156–2.175(2)	2.162–2.179(5)	2.159–2.188(4)
Co–Cp	2.06–2.07(2)	2.06(1)–2.098(8)	2.069–2.087(8)	2.074–2.098(8)	2.03–2.11(2)	2.07–2.09(2)
P–OMe	1.46–1.84(2)	1.46–1.80(2)	1.575–1.611 (6)	1.588–1.609(4)	1.58–1.60(1)	1.54–1.62(1)
P=O	1.485(8)	1.475–1.490(6)	1.490–1.499(4)	1.495–1.498(4)	1.47–1.51(1)	1.49–1.51(1)
M–O11	2.073(5)	2.067(6)	2.074(4)	2.037(3)	2.11(1)	2.09(1)
M–O21	2.023(8)	2.021(6)	2.011(3)	2.027(4)	2.10(1)	2.09(1)
M–O31	2.038(5)	2.022(7)	2.016(4)	2.019(4)	2.147(9)	2.161(9)
M–X(X)	2.109(5) (O51)	2.105(6) (O111)	2.133(4) (O2)	2.117(4) (O52)	2.372(9) (O52A)	2.30(1) (O52B)
M–O (OAr)	2.055(8) (O61)	2.043(6) (O121)	2.043(3) (O1)	2.042(4) (O51)	2.13(1) (O51A)	2.13(1) (O51B)
	2.023(5) (O61*)	2.029(7) (O121*)	2.073(3) (O1*)	2.050(4) (O51*)	2.142(9) (O51A*)	2.161(9) (O51B*)
P–Co–P	89.6–92.9(1)	89.62(9)–93.2(1)	90.64–91.93(6)	90.05–93.00(6)	91.5–92.5(2)	91.4–93.6(2)
O11–M–O21	90.3(3)	89.6(2)	91.6(1)	90.1(1)	90.6(4)	88.4(4)
O11–M–O31	93.0(2)	93.1(3)	92.7(1)	94.7(1)	90.4(4)	92.3(4)
O21–M–O31	90.6(3)	90.9(3)	93.7(1)	91.0(2)	89.4(4)	89.8(4)
O11–M–X(X)	171.2(3) (O51)	170.8(3) (O121)	173.5(1) (O1)	177.3(2) (O51)	169.2(4) (O51A)	173.8(4) (O51B)
O21–M–X(X)	94.4(3) (O51)	95.2(2) (O121)	91.4(1) (O1)	87.7(2) (O51)	91.7(4) (O51A)	91.8(4) (O51B)
O31–M–X(X)	94.3(2) (O51)	94.7(3) (O121)	92.9(1) (O1)	86.9(2) (O51)	79.1(4) (O51A)	81.4(4) (O51B)
ArO–M–OAr	80.0(2)	79.5(2)	80.6(1)	81.2(2)	80.4(4)	80.6(4)
O11–M–OAr	87.7(3) (O61)	88.0(2) (O121)	89.7(1) (O1)	100.0(1) (O51)	104.9(4) (O51A)	106.1(4) (O51B)
	87.7(2) (O61*)	87.4(3) (O121*)	89.6(1) (O1*)	91.8(1) (O51*)	99.6(3) (O51A*)	95.2(3) (O51B*)
O21–M–OAr	172.8(2) (O61)	172.2(3) (O121)	172.4(1) (O1)	169.7(1) (O51)	164.1(4) (O51A)	165.3(4) (O51B)
	93.0(3) (O61*)	93.0(2) (O121*)	91.9(1) (O1*)	96.6(2) (O51*)	93.9(4) (O51A*)	95.9(4) (O51B*)
O31–M–OAr	96.5(2) (O61)	96.6(2) (O121)	93.7(1) (O1)	90.1(2) (O51)	93.8(4) (O51A)	92.0(4) (O51B)
	176.4(3) (O61*)	176.1(2) (O121*)	173.9(1) (O1*)	169.9(1) (O51*)	169.5(4) (O51A*)	170.6(4) (O51B*)
X–M–OAr	86.7(3) (O61)	86.3(2) (O121)	86.6(1) (O1)	82.1(2) (O51)	73.6(4) (O51A)	74.1(4) (O51B)
	84.7(2) (O61*)	84.5(3) (O121*)	84.5(1) (O1*)	86.9(2) (O51*)	90.8(3) (O51A*)	91.0(3) (O51B*)

[a] Bond lengths in Å and bond angles in deg. [b] Two independent molecules. [c] Chelating *o*-NO_2 substituent of the aryloxide.

Table 3 Selected structural parameters for $[L_{OMe}M(OC_6H_4\text{-}2,6\text{-}Me_2)(X)]_2$ **5b**[a]

	5b(Ni)		**5b(Co)**		**5b(Mn)**	
Complex	Ni1[b]	Ni2[c]	Co3[b]	Co4[c]	Mn1[b]	Mn2[c]
Co–P	2.159–2.165(2)	2.163–2.168(2)	2.162–2.163(2)	2.163–2.171(2)	2.168–2.184(3)	2.171–2.184(2)
Co–Cp	2.066–2.072(9)	2.080–2.091(7)	2.068–2.082(8)	2.083–2.093(6)	2.07(1)–2.090(9)	2.079–2.096(9)
P–OMe	1.587–1.604(5)	1.596–1.608(5)	1.595–1.607(5)	1.594–1.606(4)	1.593–1.616(8)	1.585–1.615(7)
P=O	1.489–1.501(4)	1.491–1.503(4)	1.492–1.501(3)	1.488–1.501(3)	1.501–1.504(5)	1.495–1.505(5)
M–O11(41)	2.001(3)	1.994(3)	2.040(3)	2.046(3)	2.100(4)	2.107(4)
M–O21(51)	2.027(3)	2.016(3)	2.059(3)	2.053(3)	2.111(6)	2.127(6)
M–O31(61)	2.010(4)	2.017(4)	2.035(3)	2.042(3)	2.096(5)	2.112(5)
M–O1	1.977(3)	1.986(3)	1.988(3)	2.003(3)	2.073(4)	2.076(4)
M–O2	1.992(3)	1.981(3)	2.009(3)	1.998(3)	2.090(4)	2.085(4)
P–Co–P	90.06–91.92(6)	89.83–92.89(5)	90.26–92.00(5)	90.10–92.78(5)	90.96–92.92(8)	90.83–93.39(8)
O11(41)–M–O21(51)	89.6(1)	89.5(1)	87.3(1)	87.5(1)	86.6(2)	86.4(2)
O11(41)–M–O31(61)	92.9(1)	92.5(1)	92.4(1)	91.4(1)	91.2(2)	90.7(2)
O21(51)–M–O31(61)	92.7(1)	93.7(1)	92.0(1)	93.1(1)	92.1(2)	93.3(2)
O1–M–O2	77.0(1)	77.1(1)	77.9(1)	77.8(1)	77.1(2)	77.2(2)
O11(41)–M–O1	162.1(1)	91.8(1)	160.1(1)	90.3(1)	161.1(2)	90.7(2)
O11(41)–M–O2	92.4(1)	161.3(1)	90.8(1)	159.5(1)	90.6(2)	160.9(2)
O21(51)–M–O1	94.8(1)	156.9(1)	95.2(1)	152.0(1)	97.5(2)	151.0(2)
O21(51)–M–O2	157.3(2)	95.0(1)	152.5(1)	95.2(1)	151.8(2)	97.0(2)
O31(61)–M–O1	104.2(1)	109.3(1)	107.2(1)	114.9(1)	107.1(2)	115.6(2)
O31(61)–M–O2	109.7(2)	105.3(1)	115.4(1)	108.7(1)	116.0(2)	107.9(2)

[a] Bond lengths in Å and bond angles in deg. [b] O11–O31. [c] O41–O61.

their UV-vis and IR spectra. Judging from the interligand angles of **5b(Ni,Co)** the coordination geometry of the metal centers is a distorted square-pyramid with the O1–O2–O11–O21 and O1–O2–O41–O51 basal planes (Table 3). As can be seen from a bottom view of a space-filling model of **5b(Ni)** (Fig. 2b), the sixth coordination site of M1 is shielded by the two methyl groups of the aryloxo ligands to lead to a five-coordinate square-pyramidal structure. We also examined reactions with other 2,6-disubstituted aryloxides as mentioned above. Difluoro and dichloro derivatives afforded the sandwich complex **4** in a manner similar to the reactions with more basic and less hindered aryloxides, presumably because steric shielding by the halogen atoms was not effective. On the other hand, reactions with the 2,6-di-isopropyl and 2,6-di-*tert*-butyl derivatives resulted in replacement of the central metal to give the sodium salt, NaL_{OMe}. The bulkier isopropyl and *tert*-butyl groups may not fit the space formed by the dinuclear $M_2(\mu\text{-}O)_2$ core.

As will be discussed below, the manganese derivatives **5b(Mn)** and **7c(Mn)** were prepared by analogous methods. Although the molecular structures are basically the same as those of the Ni and Co counterparts, the M–O distances become longer as

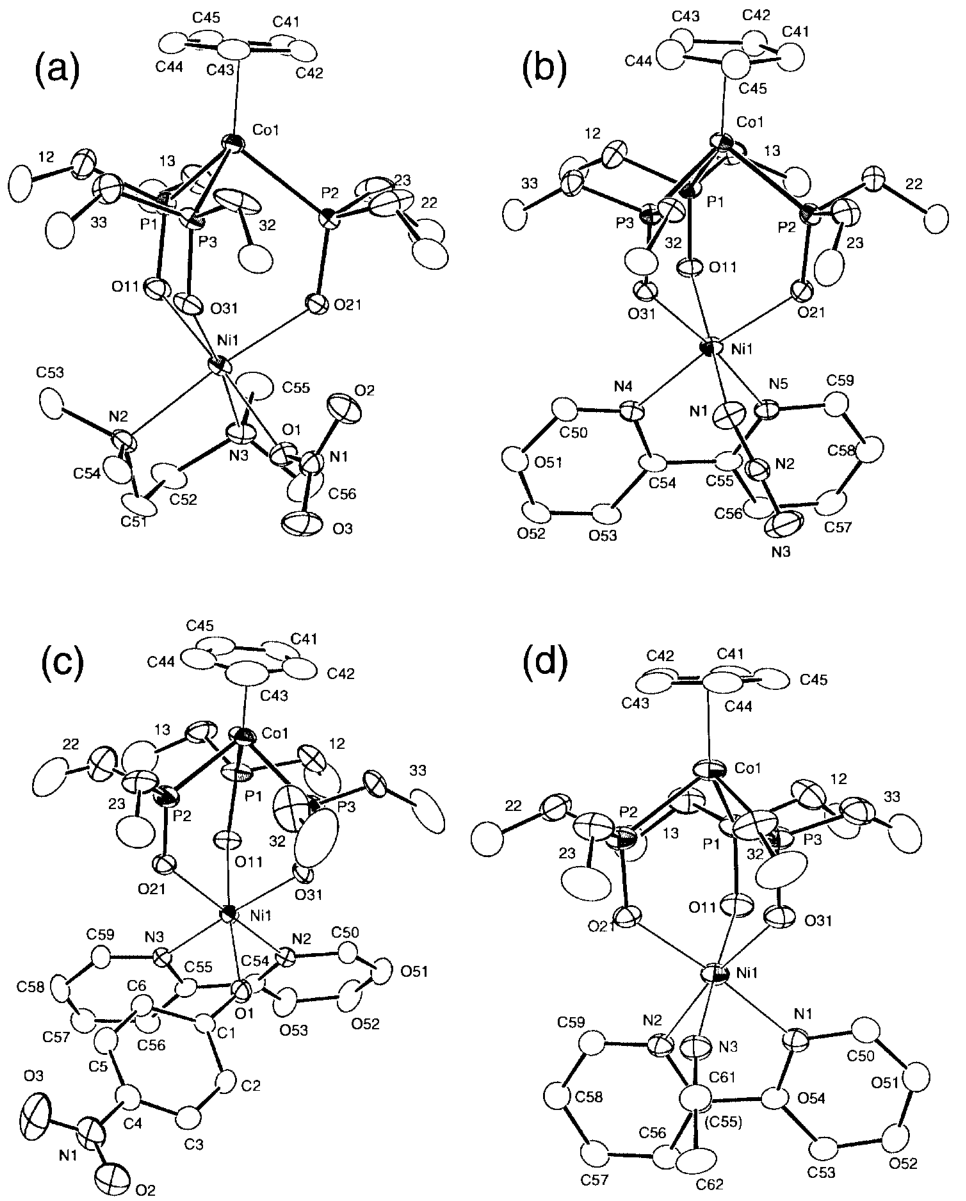


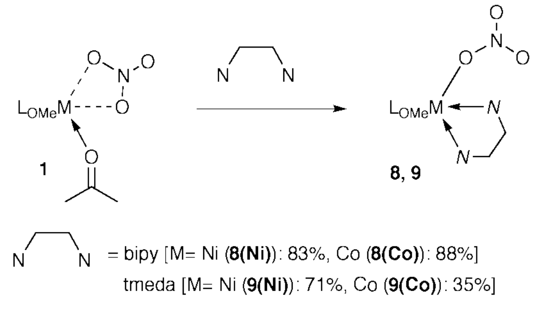
Fig. 5 Molecular structures of (a) **9(Ni)**, (b) **10**, (c) **13a** and (d) **14** drawn at the 30% probability level. Details as in Fig. 2.

going from Ni to Co and then Mn in accord with the increasing atomic radii (Table 3).[11]

In the case of complexes derived from $NaOC_6F_5$, the orange-brown five-coordinate product **5e(Ni)** was obtained for the nickel system. Exposure of **5e(Ni)** to the air led to the green, hydrated six-coordinate complex **6e(Ni)** with the aquo ligand occupying the sixth coordination site, which was characterized crystallographically (Fig. 3 and Table 2). The hydrated complex was also obtained by addition of a drop of water to **5e(Ni)**. In contrast to the Ni complexes, the five-coordinate Co species **5e(Co)** was stable and could not be converted to **6e(Co)** even by addition of water.

Reaction of complexes with bidentate ligands

The above-mentioned results indicate that the κ^1-coordinated ligand (L) in the $L_{OMe}M(L)(\kappa^2\text{-}NO_3)$ system is so labile as to be readily dissociated from the metal center[5] and, as a consequence, induce dimerization or deterioration of the $L_{OMe}M$ core. In order to prevent dissociation of the ligand (L) chelating ligands were introduced. Treatment of the nickel complex **1** with bipy and tmeda resulted in ligand replacement to give the corresponding adducts **8** and **9**, respectively (eqn. (2)). The molecular structure of the tmeda derivative **9(Ni)** determined by X-ray crystallography (Fig. 5a and Table 4) revealed that the



(2)

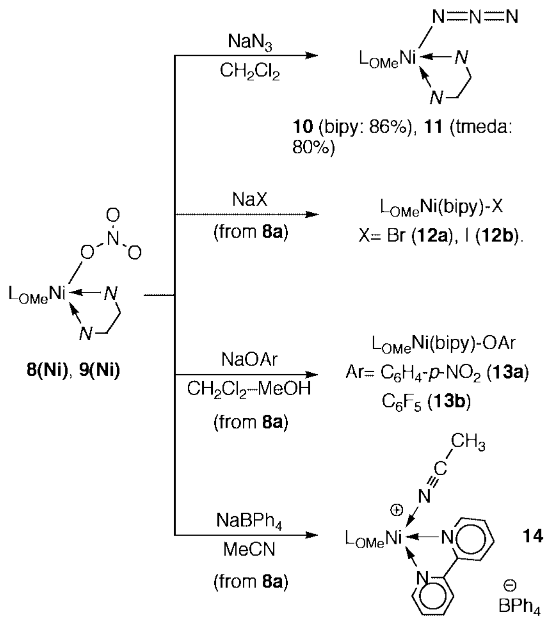
coordination mode of the nitrato ligand changed from κ^2 (**1a**) to κ^1 (**9**), and the bipy derivative **8** was also assigned to the analogous κ^1-NO_3 structure, $(L_{OMe})Ni(\kappa^2\text{-bipy})(\kappa^1\text{-}NO_3)$. Although we examined the IR data for the κ^1- and κ^3-NO_3 complexes carefully, the two coordination modes could not be differentiated by the IR features. A characteristic band around 1385 cm^{-1} assignable to $\nu(NO)$ was observed for both types of complexes.

As the first attempt of functionalization of **8(Ni)** and **9(Ni)**, synthesis of the azido complex was examined (Scheme 3). Treatment of **8(Ni)** with NaN_3 in CH_2Cl_2 readily afforded green crystals **10** and **11**, which showed $\nu(NNN)$ and $\nu(P{=}O)$

Table 4 Selected structural parameters for mononuclear complexes, $L_{OMe}Ni(L_2)X$ **9(Ni)**, **10**, **13a** and **14**[a]

Complex L_2 X	**9(Ni)** tmeda NO_3	**10** bipy N_3	**13a** bipy OC_6H_4-4-NO_2	**14** bipy MeCN
Co–P	2.158(1)–2.1660(9)	2.157(1)–2.1812(9)	2.148–2.160(2)	2.161–2.170(1)
Co–Cp	2.076–2.093(4)	2.052–2.119(9)	2.05(1)–2.074(8)	2.080–2.090(6)
P–OMe	1.577–1.601(4)	1.598–1.614(4)	1.46–1.73(1)	1.584–1.610(4)
P=O	1.489–1.501(3)	1.494–1.499(2)	1.473–1.486(4)	1.488–1.500(3)
Ni–O11	2.083(2)	2.134(3)	2.069(4)	2.050(3)
Ni–O21	2.026(2)	2.048(2)	2.079(4)	2.044(3)
Ni–O31	2.026(2)	2.041(2)	2.058(4)	2.043(3)
Ni–L_2	2.147(3)	2.067(3) (N4)	2.077(4) (N2)	2.065(3) (N1)
	2.157(3)	2.069(3) (N5)	2.076(4) (N3)	2.066(3) (N2)
Ni–X	2.182(4) (O1)	2.091(4) (N1)	2.031(4) (O1)	2.131(4) (N3)
X	1.256(5) (N1–O1)	1.163(4) (N1–N2)	1.284(6) (O1–C1)	1.131(6) (N3–C61)
	1.257(6) (N1–O2)	1.153(6) (N2–N3)		1.453(7) (C61–C62)
	1.217(6) (N1–O3)			
P–Co–P	90.65–91.21(4)	89.27–92.48(4)	90.47–91.33(8)	89.53–92.99(5)
O11–Ni–O21	91.46(9)	87.4(1)	88.1(2)	90.4(1)
O11–Ni–O31	87.4(1)	86.3(1)	90.2(2)	89.9(1)
O21–Ni–O31	92.8(1)	96.20(9)	91.6(2)	93.4(1)
O11–Ni–L_2	93.3(1) (N2)	92.3(1) (N4)	83.9(2) (N2)	89.4(1) (N1)
	89.5(1) (N3)	93.3(1) (N5)	86.9(2) (N3)	94.4(1) (N2)
O21–Ni–L_2	174.3(1) (N2)	170.3(1) (N4)	170.2(2) (N2)	172.6(1) (N1)
	92.3(1) (N3)	91.5(1) (N5)	94.9(2) (N3)	94.1(1) (N2)
O31–Ni–L_2	90.6(1) (N2)	93.4(1) (N4)	94.1(2) (N2)	94.0(1) (N1)
	174.1(1) (N3)	172.3(1) (N5)	172.8(2) (N3)	171.4(1) (N2)
O11–Ni–X	174.5(1) (O1)	173.4(1) (N1)	172.0(2) (O1)	177.8(1) (N3)
O21–Ni–X	90.8(1) (O1)	90.9(1) (N1)	99.9(2) (O1)	91.7(1) (N3)
O31–Ni–X	97.5(1) (O1)	87.5(1) (N1)	88.4(2) (O1)	89.7(1) (N3)
X–Ni–L_2	84.2(1) (O1–Ni1–N2)	90.5(1) (N1–Ni1–N4)	88.3(2) (O1–Ni1–N2)	88.5(1) (N3–Ni1–N1)
	85.4(1) (O1–Ni1–N3)	93.2(1) (N1–Ni1–N5)	93.5(2) (O1–Ni1–N3)	85.8(1) (N3–Ni1–N2)
N–Ni–N	84.6(1) (N2–Ni1–N3)	78.9(1) (N4–Ni1–N5)	79.0(2) (N2–Ni1–N3)	78.5(1) (N1–Ni1–N2)
Ni–X	137.2(3) (Ni1–O1–N1)	132.2(3) (Ni1–N1–N2)	134.2(3) (Ni1–O1–C1)	162.5(4) (Ni1–N3–C61)
	119.0(4) (O1–N1–O2)	177.7(5) (Ni–N2–N3)		178.7(5) (N3–C61–C62)
	120.1(4) (O1–N1–O3)			
	120.6(4) (O2–N1–O3)			

[a] Bond lengths in Å and bond angles in deg.



Scheme 3

vibrations at 2032 and 1142 cm^{-1} (**10**) and 2049 and 1141 cm^{-1} (**11**), respectively. Disappearance of NO_3 vibrations clearly indicated occurrence of a substitution reaction and the structure of the bipy derivative **10** was confirmed by X-ray crystallography (Fig. 5b). The coordinated nitrogen atom (N1) of the azido ligand is sp^2-hybridized as can be seen from the Ni–N–N angle (132.2(3)°) and the similar N–N distances (N1–N2: 1.163(4), N2–N3: 1.153(6) Å) (Table 4). The situation is in sharp contrast to the μ_3-N_3 ligand in **3** as discussed above.

The nitrate complex **8** was found to be converted into halide complexes **12** upon treatment with NaX.

Aryloxo complexes **13** were prepared by treatment with sodium aryloxide, and the 4-NO_2 derivative **13a** was characterized by X-ray crystallography (Fig. 5c). Although the structural features of the L_{OMe}Ni–O part are similar to those of the other OC_6H_4-NO_2 derivatives **6d(Ni)** and **7c(Ni)**, the aryl moieties are considerably distorted. The structural parameters are compared as shown in Chart 2. The C–C lengths of the aromatic ring in **6d(Ni)** are in the narrow range between 1.36–1.40 Å, whereas those for **13a** and **7c(Ni)** are in the ranges 1.34–1.425 Å and 1.33–1.425 Å, respectively. In addition, bond alternation is much more evident for **13a** and **7c(Ni)** and indicates contribution of *p*- (**C**) and *o*-quinoid resonance forms (**D**),

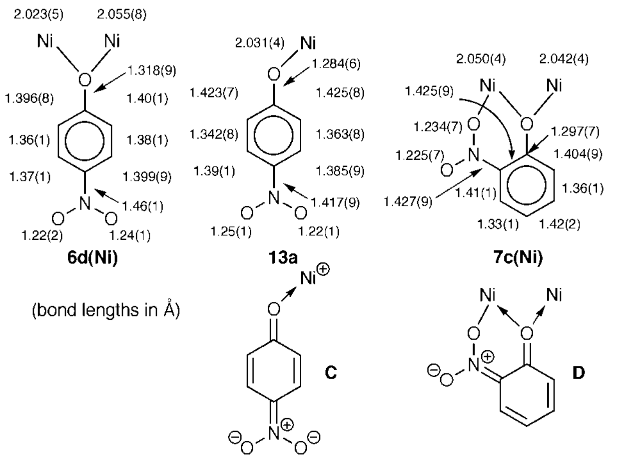
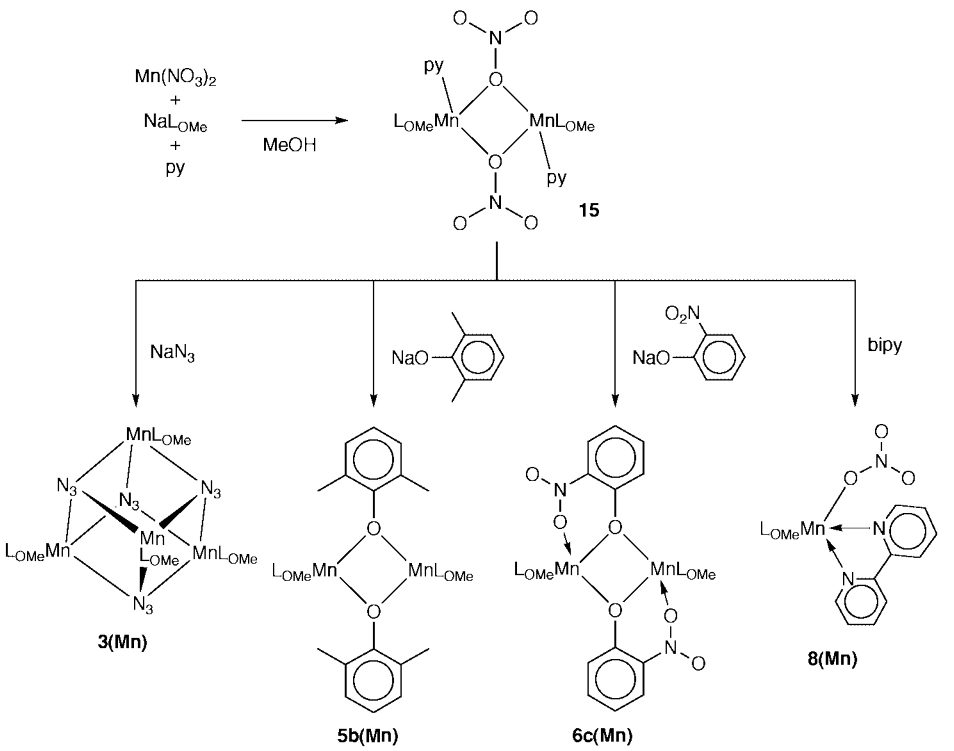


Chart 2



Scheme 4

respectively. In accord with this consideration, the C–O and C–N distances in the aryl moieties of **13a** and **7c(Ni)** are substantially shorter than those in **6d(Ni)**. Reaction of **8** with other aryloxides such as $NaOC_6H_5$ and $NaOC_6H_3$-2,6-Me_2 resulted in the formation of $(L_{OMe})_2Ni$, and reaction with NaOH and NaOMe[8] caused demetalation from the L_{OMe} ligand to give $L_{OMe}Na$ as revealed by ^{1}H-NMR analysis of the obtained residues.

Furthermore the nitrate ligand in **8(Ni)** was found to be labile enough to be ionized in MeCN to give the solvent-stabilized cationic species **14**, which was also confirmed by X-ray crystallography (Fig. 5d). In contrast to the bent structure of the Ni–N_3 moiety in **10** (Chart 1), the Ni1–N3–C61 angle (162.5(4)°) supports the sp-hybridization of the coordinated nitrogen atom (N3) in the acetonitrile ligand.

Synthesis of manganese complexes

In order to further study $L_{OMe}M$ complexes of divalent metal species synthesis of Mn complexes was examined.[12]

We attempted synthesis of **1**-type starting compounds of manganese following the procedure similar to those for the Ni and Co complexes[5] but a pure sample could not be obtained. Then a donor-stabilized **2**-type complex with pyridine ligand was prepared by mixing the three components (Scheme 4). The obtained yellow pyridine adduct **15**, however, was not a mononuclear complex but a dinuclear μ-NO_3 complex as revealed by preliminary X-ray crystallography. Due to the larger atomic radius of Mn compared to Co and Ni, the NO_3 ligand may prefer the bridging κ^1-coordination to the strained cyclic κ^2-coordination as found for **1(Ni, Co)**.[5] The pyridine moiety was also found to be labile. For example, addition of NaN_3 afforded the cubane-like tetrameric complex **3(Mn)**, which was characterized on the basis of the IR and analytical data. Some additional representative transformations similar to the Ni and Co systems were also examined. Treatment of **15** with aryloxide anions afforded μ-aryloxo complexes **5b(Mn)** and **7c(Mn)**, and addition of bipy resulted in ligand replacement to give the mononuclear complex **8(Mn)**. Further reaction of **15** and **8(Mn)** with NaOH gave the sandwich complex **4(Mn)**[9] as the sole isolable product.

Conclusion

Reaction of the labile complexes with the Kläui tripodal ligand, $L_{OMe}M(L)(\kappa^2\text{-}NO_3)$ (M = Ni, Co; L = acetone, PPh_3), with various anionic nucleophiles results not only in substitution of the nitrato ligand but also labilization of L. As a result, a variety of oligomeric products including tetranuclear tetrakis(μ_3-azido) complexes and dinuclear μ-aryloxo complexes are obtained. Substitution of the κ^2-coordinated nitrato ligand by an anionic 2e-donor leaves a coordinatively unsaturated site, which interacts with an electron pair in another molecule of the unsaturated species to form the oligomeric structures. Mononuclear complexes are obtained only from $L_{OMe}M(\kappa^2\text{-}L)(\kappa^1\text{-}NO_3)$ with bidentate ligands (κ^2-L: bipy, tmeda). Unfortunately sandwich complexes $(L_{OMe})_2M$ are frequently formed *via* disproportionation of the L_{OMe} complexes, and this undesired reaction becomes a major reaction pathway in the case of reaction with strong donors such as hydroxide and alkoxide as well as reaction in the presence of water.

Kläui mentioned that the L_{OR} fragment is a good π-electron donor compared to cyclopentadienyls and polypyrazolylborates.[1] In the case of complexes bearing strong donors, electrostatic repulsion between the negative charges on the metal center and the α-heteroatom of the ligand may cause labilization of the complexes. Electron-withdrawing substituents in the incoming ligand such as C_6F_5 and $C_6H_4NO_2$ may be required to reduce electron density at the coordinated heteroatom. Many $L_{OR}M(X)_n$-type half-sandwich complexes of main group elements and second and third row transition metals have been reported so far, whereas few examples of first row metal complexes have been isolated except the full-sandwich complexes, $(L_{OR})_2M$.[4] The present work has opened the way to the study of first row metal half-sandwich complexes bearing the Kläui oxygen tripodal ligand, though some problems remain.

Experimental

General methods

All manipulations were carried out under an inert atmosphere by using standard Schlenk techniques. MeOH ($Mg(OMe)_2$),

CH_2Cl_2 (P_4O_{10}), THF and ether (Na–K/benzophenone), were treated with appropriate drying agents, distilled, and stored under argon. IR (as KBr pellets) and UV-vis spectra (CH_2Cl_2 solutions unless otherwise stated) were obtained on a JASCO FT/IR 5300 spectrometer and a Shimadzu UV-260 spectrometer, respectively. Starting complexes were prepared according to our previous paper.[5] Sodium aryloxides (substituted phenoxides) were obtained by dropwise addition of ethereal solutions of the corresponding phenols to an ether suspension of NaH followed by collection by filtration, washing with ether and drying under reduced pressure. They could be generated *in situ* and used without purification (see below). Other chemicals were used as received without further purification.

Preparations

(L_{OMe}Ni)$_4$(μ_3-N_3)$_4$ 3(Ni). *(i) From* **1(Ni)**. An equimolar mixture of **1(Ni)** (181 mg, 0.286 mmol) and NaN_3 (19 mg, 0.286 mmol) in CH_2Cl_2 (8 mL) was stirred overnight at ambient temperature. Insoluble materials were removed by filtration through a Celite pad and cooling of the filtrate at −30 °C gave **3** as yellow crystals (134 mg, 0.063 mmol, 88% yield). UV-vis (λ_{max}/nm, ε/M^{-1} cm^{-1}; in CH_2Cl_2): 244 (1.22×10^5), 334 (1.59×10^4), 706 (19.5), 765 (18.1). IR (cm^{-1}; KBr) 2988 (sh), 2948 (m), 2841 (w), 2084 (vs, ν_{N_3}), 1629 (w), 1460 (w), 1377 (w), 1325 (w), 1260 (w), 1180 (sh), 1134 (vs, $\nu_{P=O}$), 1102 (w), 1033 (vs), 1004 (vs), 834 (s), 773 (s), 724 (s), 592 (s, $\delta_{P=O}$). Anal. Calc. for $C_{44}H_{92}N_{12}O_{36}P_{12}Co_4Ni_4$: C, 23.94; H, 4.20; N, 7.61. Found: C, 23.17; H, 4.11; N, 7.37%.

(ii) From **2(Ni)**. A mixture of **2(Ni)** (196 mg, 0.235 mmol) and NaN_3 (18 mg, 0.281 mmol) in CH_2Cl_2 (8 mL) was stirred overnight and worked up as described above. **3** (89 mg, 0.041 mmol, 69% yield).

(L_{OMe}Co)$_4$(μ_3-N_3)$_4$ 3(Co). To a CH_2Cl_2 (5 mL) solution of **1(Co)** (170 mg, 0.270 mmol) was added NaN_3 (53 mg, 0.811 mmol) and the resultant mixture was stirred for 24 h at ambient temperature. The pink product was collected on a glass frit, washed with water and a minimum amount of MeOH, and dried under reduced pressure. **3(Co)** (133 mg, 0.060 mmol, 89% yield): UV-vis (λ_{max}/nm, ε/M^{-1} cm^{-1}; in CH_2Cl_2): 245 (1.54×10^5), 336 (2.05×10^4), 500 (70.8, sh), 552 (129.2). IR (cm^{-1}; KBr) 3119 (w), 2984 (sh), 2948 (m), 2841 (m), 2081 (vs, ν_{N_3}), 1459 (w), 1426 (w), 1319 (w), 1253 (w), 1180 (sh), 1137 (vs, $\nu_{P=O}$), 1043 (vs), 1009 (vs), 834 (m), 774 (s), 723 (s), 645 (sh), 586 (s, $\delta_{P=O}$). Anal. Calc. for $C_{44}H_{92}N_{12}O_{36}P_{12}Co_8$: C, 23.93; H, 4.20; N, 7.61. Found: C, 23.82; H, 4.08; N, 7.81%.

[L_{OMe}Ni(OC_6H_2-2,4,6-Me_3)]$_2$ 5a(Ni). This complex was prepared according to a similar procedure to the synthesis of **5b(Ni)** (see below). **5a(Ni)** (pink prism; 36% yield): UV-vis (λ_{max}/nm, ε/M^{-1} cm^{-1}; in CH_2Cl_2): 244 (6.89×10^4), 335 (9.21×10^3), 528 (36.5), 580 (11.4), 730 (18.5), 819 (41.9). IR (cm^{-1}; KBr) 2987 (sh), 2909 (sh), 2838 (w), 1480 (m), 1426 (w), 1306 (w), 1244 (m), 1136 (vs, $\nu_{P=O}$), 1094 (w), 1036 (vs), 1008 (vs), 852 (w), 837 (w), 798 (sh), 771 (s), 728 (s), 602 (s, $\delta_{P=O}$). Anal. Calc. for $C_{40}H_{68}N_2O_{20}P_6Co_2Ni_2$: C, 37.21; H, 5.31. Found: C, 37.08; H, 5.40%.

[L_{OMe}Ni(OC_6H_3-2,6-Me_2)]$_2$ 5b(Ni). *(i) From* **1(Ni)**. To a THF solution (8 mL) of **1(Ni)** (283 mg, 0.449 mmol) was added $NaOC_6H_3$-2,6-Me_2 (40 mg, 0.28 mmol) dissolved in THF (24 mL) dropwise at room temperature. The color of the mixture changed from green to orange-brown and colorless precipitates appeared immediately. After the mixture was stirred overnight, the volatiles were removed under reduced pressure, and the residue was extracted with CH_2Cl_2 and filtered through a Celite pad. Concentration of the volume to *ca.* 3 mL and addition of ether followed by cooling at −30 °C gave **5b(Ni)** as orange-brown crystals (183 mg, 0.136 mmol, 60% yield). UV-vis (λ_{max}/nm, ε/M^{-1} cm^{-1}; in CH_2Cl_2): 244 (9.37×10^4), 337 (1.28×10^4), 526 (23.1), 580 (6.4), 730 (11.5), 822 (28.2). IR (cm^{-1}; KBr) 3128 (w), 2988 (sh), 2946 (s), 2839 (m), 1587 (m), 1468 (s), 1427 (s), 1268 (s), 1233 (s), 1176 (sh), 1136 (vs, $\nu_{P=O}$), 1092 (m), 1035 (vs), 1007 (vs), 848 (s), 835 (s), 773 (vs), 728 (vs), 689 (sh), 625 (sh), 596 (s, $\delta_{P=O}$). Anal. Calc. for $C_{39}H_{66}O_{20}P_6Cl_2Co_2Ni_2$: C, 34.78; H, 4.94; N, 5.26. Found: C, 34.61; H, 4.93; N, 5.49%.

(ii) From **2(Ni)**. To a THF solution (10 mL) of **2(Ni)** (235 mg, 0.282 mmol) was added $NaOC_6H_3$-2,6-Me_2 (48 mg, 0.338 mmol) dissolved in THF (20 mL) dropwise at room temperature. The color of the mixture changed from green to orange-brown and the mixture was stirred overnight. Then the volatiles were removed under reduced pressure, and the residue was extracted with CH_2Cl_2 and filtered through a Celite pad. Concentration of the volume to *ca.* 3 mL and addition of ether followed by cooling at −30 °C gave **5b(Ni)** as orange-brown crystals (139 mg, 0.103 mmol, 73% yield).

[L_{OMe}Ni(OC_6H_4-2-NO_2)]$_2$ 7c(Ni). To a THF solution (10 mL) of **2(Ni)** (212 mg, 0.254 mmol) was added $NaOC_6H_4$-2-NO_2 (49 mg, 0.306 mmol) dissolved in THF (15 mL) dropwise at room temperature. The resultant mixture was stirred for 30 min and then filtered through a Celite pad to give a deep red brown solution. The filtrate was evaporated under reduced pressure, and the residue was extracted with CH_2Cl_2. Filtration through a Celite pad and addition of ether followed by cooling at −30 °C gave **7c(Ni)** as red-brown crystals (111 mg, 0.086 mmol, 68% yield). UV-vis (λ_{max}/nm, ε/M^{-1} cm^{-1}; in CH_2Cl_2): 243 (1.35×10^5), 340 (2.48×10^4), 429 (3.43×10^3), 694 (10.9), 777 (12.3). IR (cm^{-1}; KBr) 2989 (sh), 2947 (s), 2843 (w), 1601 (s), 1557 (s), 1495 (s), 1462 (sh), 1428 (w), 1347 (s), 1333 (s), 1253 (s), 1134 (vs, $\nu_{P=O}$), 1100 (w), 1028 (s), 1004 (s), 886 (w), 854 (w), 831 (m), 771 (s), 751 (m), 726 (s), 625 (s), 601 (s, $\delta_{P=O}$). Anal. Calc. for $C_{34}H_{54}N_2O_{24}P_6Co_2Ni_2$: C, 31.51; H, 4.20; N, 2.16. Found: C, 31.35; H, 3.87; N, 2.08%.

[L_{OMe}Ni(OC_6H_4-4-NO_2)(MeOH)]$_2$ 6d(Ni). To a THF solution (8 mL) of **2(Ni)** (203 mg, 0.243 mmol) was added $NaOC_6H_4$-4-NO_2 (47 mg, 0.289 mmol) dissolved in MeOH (8 mL) and THF (12 mL) dropwise at room temperature. The color of the solution changed from green to orange-yellow immediately and the mixture was stirred overnight. Then the volatiles were removed under reduced pressure, and the residue was extracted with CH_2Cl_2 and filtered through a Celite pad. Concentration of the volume to *ca.* 3 mL and addition of ether followed by cooling at −30 °C gave **6d(Ni)** as orange-brown crystals (120 mg, 0.079 mmol, 65% yield). UV-vis (λ_{max}/nm, ε/M^{-1} cm^{-1}; in CH_2Cl_2): 242 (1.06×10^5), 334 (1.89×10^4), 411 (3.19×10^4), 692 (14.2), 761 (16.6). IR (cm^{-1}; KBr) 3589 (m), 2981 (sh), 2946 (m), 2896 (sh), 2839 (w), 1578 (s), 1494 (s), 1481 (s), 1427 (w), 1334 (sh), 1287 (vs), 1168 (w), 1136 (vs, $\nu_{P=O}$), 1109 (s), 1090 (w), 1035 (vs), 1006 (vs), 861 (m), 829 (m), 773 (s), 725 (s), 647 (m), 624 (sh), 596 (s, $\delta_{P=O}$). Anal. Calc. for $C_{38}H_{66}N_2O_{26}P_6Cl_4Co_2Ni_2$: C, 29.83; H, 4.85; N, 1.83. Found: C, 29.76; H, 4.10; N, 2.10%.

[L_{OMe}Ni(OC_6F_5)]$_2$ 5e(Ni). To a THF solution (8 mL) of **2(Ni)** (218 mg, 0.262 mmol) was added $NaOC_6F_5$ (59 mg, 0.287 mmol) dissolved in THF (16 mL) dropwise at room temperature. Colorless precipitates appeared and the mixture was stirred overnight. Then the volatiles were removed under reduced pressure, and the residue was extracted with CH_2Cl_2 and filtered through a Celite pad. Concentration of the volume to *ca.* 3 mL and addition of ether followed by cooling at −30 °C gave **5e(Ni)** as orange-brown crystals (76 mg, 0.106 mmol, 41% yield). UV-vis (λ_{max}/nm, ε/M^{-1} cm^{-1}; in CH_2Cl_2): 241 (8.85×10^4), 333 (1.04×10^4), 703 (10.6), 809 (18.6). IR (cm^{-1}; KBr) 2949 (s), 2846 (w), 1618 (m), 1503 (vs), 1476 (sh), 1133 (vs, $\nu_{P=O}$), 1042 (vs), 1011 (vs), 836 (m), 775 (vs), 729 (s), 624 (sh), 591 (s, $\delta_{P=O}$). Anal. Calc. for $C_{34}H_{50}O_{22}F_{10}P_6Co_2Ni_2$: C, 28.72; H, 3.54; F, 13.36. Found: C, 28.55; H, 3.57; F, 13.12%.

$[\mathrm{L_{OMe}Ni(OC_6F_5)(H_2O)}]_2$ 6e(Ni). When **5e(Ni)** dissolved in a mixture of THF–ether was exposed to the air for several days, green crystals of **6e(Ni)** were grown. **6e(Ni)** was also obtained by addition of a drop of water to a THF solution of **5e(Ni)**. **6e(Ni)**: UV-vis (λ_{max}/nm, ε/M^{-1} cm^{-1}; in CH_2Cl_2): 241 (9.05×10^4), 333 (1.08×10^4), 712 (7.6), 782 (11.9). IR (cm^{-1}; KBr) 3643 (s, ν_{H_2O}), 3132 (w), 2990 (sh), 2948 (s), 2901 (sh), 2843 (w), 1625 (w), 1505 (vs), 1477 (m), 1426 (sh), 1308 (w), 1246 (w), 1170 (sh), 1134 (vs, $\nu_{P=O}$), 1085 (w), 1040 (vs), 1011 (vs), 835 (s), 774 (vs), 730 (vs), 625 (sh), 593 (s, $\delta_{P=O}$). Anal. Calc. for $C_{34}H_{50}O_{22}F_{10}P_6Co_2Ni_2$: C, 28.72; H, 3.54; F, 13.36. Found: C, 28.55; H, 3.57; F, 13.12%.

$[\mathrm{L_{OMe}Co(OC_6H_2\text{-}2,4,6\text{-}Me_3)}]_2$ 5a(Co). This complex was prepared according to a similar procedure to the synthesis of **5a(Ni)** (see above). **5a(Co)** (red brown prisms, 42% yield). UV-vis (λ_{max}/nm, ε/M^{-1} cm^{-1}; in CH_2Cl_2): 243 (1.00×10^5), 292 (2.07×10^4), 334 (1.42×10^3), 464 (122), 524 (59.9), 586 (154.1), 825 (11.9). IR (cm^{-1}; KBr) 2986 (sh), 2945 (m), 2908 (sh), 2842 (w), 1479 (m), 1426 (m), 1368 (m), 1241 (s), 1138 (vs, $\nu_{P=O}$), 1088 (w), 1037 (vs), 1004 (vs), 850 (m), 831 (m), 798 (sh), 772 (s), 621 (sh), 592 (s, $\delta_{P=O}$). Anal. Calc. for $C_{40}H_{68}O_{20}P_6Co_4$: C, 37.22; H, 5.31. Found: C, 36.89; H, 5.02%.

$[\mathrm{L_{OMe}Co(OC_6H_3\text{-}2,6\text{-}Me_2)}]_2$ 5b(Co). To a THF solution (10 mL) of **1b** (176 mg, 0.279 mmol) was added $NaOC_6H_3$-2,6-Me_2 (40 mg, 0.280 mmol) dissolved in THF (15 mL) dropwise at room temperature. The color of the mixture changed from green to orange-brown and colorless precipitates appeared immediately. After the mixture was stirred overnight, the volatiles were removed under reduced pressure, and the residue was extracted with CH_2Cl_2 and filtered through a Celite pad. Concentration under reduced pressure and addition of ether followed by cooling at −30 °C gave **5b(Co)** as orange-brown crystals (95 mg, 0.071 mmol, 51% yield). UV-vis (λ_{max}/nm, ε/M^{-1} cm^{-1}; in CH_2Cl_2): 243 (6.67×10^4), 337 (8.35×10^4), 471 (121.4), 524 (63.3), 588 (163), 825 (12.3). IR (cm^{-1}; KBr) 2992 (sh), 2946 (m), 901 (s), 2839 (m), 1588 (w), 1468 (m), 1426 (m), 1371 (w), 1268 (vs), 1232 (vs), 1175 (sh), 1138 (vs, $\nu_{P=O}$), 1090 (w), 1033 (vs), 1003 (vs), 845 (m), 835 (m), 772 (s), 726 (s), 688 (w), 624 (sh), 593 (s, $\delta_{P=O}$). Anal. Calc. for $C_{39}H_{66}O_{20}P_6Cl_2Co_4$: C, 34.77; H, 4.94; Cl, 5.26. Found: C, 34.64; H, 5.09; Cl, 4.89%.

$[\mathrm{L_{OMe}Co(OC_6F_5)}]_2$ 5e(Co). To a THF solution (15 mL) of **1(Co)** (186 mg, 0.294 mmol) was added $NaOC_6F_5$ (67 mg, 0.327 mmol) dissolved in THF (15 mL) dropwise at room temperature. Colorless precipitates appeared and the mixture was stirred for 5 h. Then the mixture was filtered and the filtrate was evaporated under reduced pressure. Extraction with CH_2Cl_2, filtration through a Celite pad, and the volatiles were removed again under reduced pressure. Crystallization of the residue from THF–ether gave **5e(Co)** as purple-red powder (109 mg, 0.0785 mmol, 53% yield). UV-vis (λ_{max}/nm, ε/M^{-1} cm^{-1}; in CH_2Cl_2): 240 (8.41×10^4), 334 (1.14×10^4), 486 (92.0), 529 (74.4), 589 (145.0), 670 (13.8, sh), 875 (12.5). IR (cm^{-1}; KBr) 3135 (w), 2946 (m), 2901 (sh), 2837 (w), 1504 (vs), 1477 (m), 1426 (w), 1310 (w), 1162 (sh), 1125 (vs, $\nu_{P=O}$), 1042 (vs), 1004 (vs), 834 (m), 771 (s), 728 (s), 624 (sh), 591 (s, $\delta_{P=O}$). Anal. Calc. for $C_{34}H_{46}O_{20}F_{10}P_6Co_4$: C, 29.46; H, 3.34; F, 13.20. Found: C, 29.59; H, 3.61; F, 12.99%.

$[\mathrm{L_{OMe}Co(OC_6H_4\text{-}2\text{-}NO_2)}]_2$ 7c(Co). This complex was prepared according to a similar procedure to the synthesis of **7c(Ni)** (see above). **7c(Co)** (red-brown prism; 64% yield): UV-vis (λ_{max}/nm, ε/M^{-1} cm^{-1}; in CH_2Cl_2): 242 (8.11×10^4), 338 (1.20×10^4), 430 (5.02×10^3, sh). IR (cm^{-1}; KBr) 2946 (m), 2841 (w), 1601 (s), 1557 (m), 1497 (s), 1463 (w), 1428 (w), 1345 (s), 1336 (s), 1254 (s), 1133 (vs, $\nu_{P=O}$), 1095 (w), 1030 (vs), 1009 (vs), 883 (w), 833 (m), 771 (s), 752 (sh), 726 (s), 623 (sh), 598 (s, $\delta_{P=O}$). Anal. Calc. for $C_{34}H_{54}N_2O_{24}P_6Co_4$: C, 31.50; H, 4.20; N, 2.16. Found: C, 31.26; H, 4.21; N, 2.17%.

$\mathrm{L_{OMe}Ni(bipy)(\kappa^1\text{-}NO_3)}$ 8(Ni). Upon addition of bipy (38 mg, 0.244 mmol) to a CH_2Cl_2 solution (5 mL) of **1(Ni)** (154 mg, 0.244 mmol) the solution color changed from yellowish green to green immediately and green solid gradually precipitated out from the solution. The resultant mixture was stirred overnight. Ether (5 mL) was added to precipitate the product, which was collected on a glass frit and dried under reduced pressure. **8(Ni)** (148 mg, 0.204 mmol, 83% yield) as green crystals. UV-vis (λ_{max}/nm, ε/M^{-1} cm^{-1}; in CH_2Cl_2): 243 (3.63×10^4), 294 (1.37×10^4), 302 (1.55×10^4), 334 (3.47×10^3), 628 (6.6), 745 (3.9). IR (cm^{-1}; KBr) 3047 (w), 2985 (w), 2945 (m), 2837 (w), 1607 (m), 1597 (m), 1474 (w), 1444 (w), 1385 (s), 1314 (m), 1263 (w), 1149 (vs, $\nu_{P=O}$), 1028 (vs), 1004 (vs), 832 (m), 766 (s), 723 (s), 620 (w), 588 (s, $\delta_{P=O}$). Anal. Calc. for $C_{21}H_{31}N_3O_{12}P_3CoNi$: C, 34.65; H, 4.29; N, 5.77. Found: C, 34.29; H, 4.19; N, 5.69%.

$\mathrm{L_{OMe}Ni(tmeda)(\kappa^1\text{-}NO_3)}$ 9(Ni). Upon addition of tmeda (29 mg, 0.215 mmol) to a CH_2Cl_2 solution (6 mL) of **1(Ni)** (135 mg, 0.215 mmol) the solution color changed to green immediately. The resultant mixture was stirred overnight. Concentration to a *ca.* 1/3 volume under reduced pressure, addition of ether and cooling at −30 °C gave **9(Ni)** (195 mg, 0.152 mmol, 71% yield) as green crystals. UV-vis (λ_{max}/nm, ε/M^{-1} cm^{-1}; in CH_2Cl_2): 242 (4.74×10^4), 303 (6.15×10^3), 329 (7.42×10^3), 694 (8.0), 790 (4.2). IR (cm^{-1}; KBr) 3107 (w), 3014 (w), 2977 (w), 2947 (s), 2893 (w), 2837 (m), 1654 (w), 1474 (m), 1385 (s), 1317 (s), 1139 (vs, $\nu_{P=O}$), 1051 (s), 1007 (vs), 847 (m), 807 (m), 769 (s), 723 (s), 583 (s, $\delta_{P=O}$). Anal. Calc. for $C_{17}H_{39}N_3O_{12}P_3CoNi$: C, 29.68; H, 5.71; N, 6.11. Found: C, 29.48; H, 5.48; N, 5.96%.

$\mathrm{L_{OMe}Co(bipy)(\kappa^1\text{-}NO_3)}$ 8(Co). This complex was prepared according to a similar procedure to the synthesis of **8(Ni)** (see above). **8(Co)** (pink powder, 88% yield). UV-vis (λ_{max}/nm, ε/M^{-1} cm^{-1}; in CH_2Cl_2): 208 (4.86×10^4), 241 (5.31×10^4), 292 (2.07×10^4), 334 (6.53×10^3), 470 (26.8), 510 (20.9). IR (cm^{-1}; KBr) 2977 (sh), 2946 (m), 2837 (w), 1604 (m), 1564 (w), 1437 (sh), 1443 (s), 1407 (s), 1384 (s), 1301 (s), 1136 (vs, $\delta_{P=O}$), 1031 (vs), 1004 (vs), 832 (m), 766 (s), 736 (s), 652 (m), 617 (m), 583 (s, $\delta_{P=O}$). Anal. Calc. for $C_{21}H_{31}N_3O_{12}P_3Co_2$: C, 34.63; H, 4.29; N, 5.77. Found: C, 34.54; H, 4.33; N, 5.55%.

$\mathrm{L_{OMe}Co(tmeda)(\kappa^1\text{-}NO_3)}$ 9(Co). This complex was prepared according to a similar procedure to the synthesis of **9(Ni)** (see above). **9(Co)** (red prism, 35% yield). UV-vis (λ_{max}/nm, ε/M^{-1} cm^{-1}; in CH_2Cl_2): 242 (4.46×10^4), 336 (4.36×10^3), 505 (13.2), 531 (15.1), 545 (15.0), 567 (12.6). IR (cm^{-1}; KBr) 3117 (sh), 3010 (sh), 2948 (m), 2892 (w), 2840 (m), 1652 (br w), 1475 (s), 1384 (vs), 1138 (vs, $\nu_{P=O}$), 1100 (w), 1041 (vs), 1001 (vs), 954 (sh), 849 (w), 830 (m), 802 (m), 773 (s), 723 (s), 617 (sh), 583 (s, $\delta_{P=O}$). Anal. Calc. for $C_{17}H_{39}N_3O_{12}P_3Co_2$: C, 29.67; H, 5.71; N, 6.11. Found: C, 29.22; H, 5.68; N, 5.81%.

$\mathrm{L_{OMe}Ni(bipy)(\kappa^1\text{-}N_3)}$ 10. NaN_3 (28 mg, 0.43 mmol) was suspended in a CH_2Cl_2 solution (10 mL) of **8(Ni)** (105 mg, 0.144 mmol) and the mixture was stirred overnight at room temperature. The reaction mixture was passed through a Celite pad to remove the inorganic salts and the filtrate was evaporated under reduced pressure. The residue was crystallized from MeOH–ether at −30 °C to give **10** (88 mg, 0.125 mmol, 86% yield) as green crystals. UV-vis (λ_{max}/nm, ε/M^{-1} cm^{-1}; in CH_2Cl_2): 244 (3.84×10^4), 293 (1.65×10^4), 302 (1.72×10^4), 330 (4.86×10^3), 638 (8.8), 770 (3.2). IR (cm^{-1}; KBr) 3060 (w), 2977 (w), 2944 (m), 2837 (w), 2032 (vs, ν_{N_3}), 1599 (m), 1473 (m), 1446 (m), 1321 (w), 1142 (vs, $\nu_{P=O}$), 1033 (vs), 1005 (vs), 829 (m), 763 (s), 721 (s), 653 (w), 575 (s, $\delta_{P=O}$). Anal. Calc. for $C_{21}H_{31}N_5O_9P_3CoNi$: C, 35.62; H, 4.41; N, 9.89. Found: C, 35.39; H, 4.48; N, 9.96%.

L_{OMe}Ni(tmeda)(κ^1-N_3) 11. This complex was prepared according to a similar procedure to the synthesis of **10** (see above). **11** (green prisms, 80% yield). UV-vis (λ_{max}/nm, ε/M^{-1} cm^{-1}; in CH_2Cl_2): 242 (3.97×10^4), 302 (5.96×10^3), 335 (6.07×10^3), 678 (9.4), 780 (4.9). IR (cm^{-1}; KBr) 2977 (sh), 2943 (m), 2874 (m), 2835 (m), 2049 (vs, ν_{N_3}), 1459 (m), 1286 (w), 1141 (vs, $\nu_{P=O}$), 1095 (w), 1051 (vs), 1008 (vs), 830 (m), 805 (m), 768 (s), 719 (s), 578 (s, $\delta_{P=O}$). Anal. Calc. for $C_{17}H_{39}N_5O_9P_3CoNi$: C, 30.56; H, 5.88; N, 10.48. Found: C, 30.31; H, 5.96; N, 10.34%.

L_{OMe}Ni(bipy)-Br 12a. This complex was prepared according to a similar procedure to the synthesis of **10** (see above). **12a** (green powder, 75% yield). UV-vis (λ_{max}/nm, ε/M^{-1} cm^{-1}; in CH_2Cl_2): 245 (4.15×10^4), 293 (1.87×10^4), 301 (1.78×10^4), 333 (3.88×10^3), 654 (6.0), 770 (2.7, sh). IR (cm^{-1}; KBr) 2944 (m), 2837 (w), 1597 (m), 1443 (m), 1384 (m), 1321 (w), 1265 (w), 1148 (vs, $\nu_{P=O}$), 1028 (vs), 1005 (vs), 932 (m), 766 (s), 722 (s), 590 (s, $\delta_{P=O}$). Anal. Calc. for $C_{21}H_{31}N_2O_9P_3CoNiBr$: C, 33.81; H, 4.19; N, 3.76. Found: C, 33.17; H, 4.18; N, 3.94%.

L_{OMe}Ni(bipy)-I 12b. This complex was prepared according to a similar procedure to the synthesis of **10** (see above). **12b** (green powder, 83% yield). UV-vis (λ_{max}/nm, ε/M^{-1} cm^{-1}; in CH_2Cl_2): 244 (4.63×10^4), 294 (1.62×10^4), 302 (1.73×10^4), 333 (4.54×10^3), 638 (6.6), 745 (3.4, sh). IR (cm^{-1}; KBr) 2944 (m), 2828 (w), 1599 (m), 1468 (m), 1446 (s), 1384 (m), 1312 (m), 1262 (m), 1135 (vs, $\nu_{P=O}$), 1028 (vs), 1005 (vs), 833 (m), 766 (s), 723 (s), 655 (m), 623 (m), 580 (s, $\delta_{P=O}$). Anal. Calc. for $C_{21}H_{31}N_2O_9P_3CoNiI$: C, 31.81; H, 3.94; N, 3.53; I, 16.00. Found: C, 32.13; H, 4.29; N, 3.90; I, 16.31%.

L_{OMe}Ni(bipy)-OC_6H_4-4-NO_2 13a. A MeOH solution of $NaOC_6H_4$-4-NO_2 was prepared by successive addition of MeOH (5 mL) and HOC_6H_4-4-NO_2 (28 mg, 0.20 mmol). (**CAUTION**: MeOH should be added with great care, because it may cause vigorous formation of H_2 gas.) To the resulting solution was added **8(Ni)** (144 mg, 0.198 mmol) dissolved in CH_2Cl_2 (8 mL) and the mixture was stirred for 5 h at rt. Then the volatiles were removed under reduced pressure and the residue was extracted with CH_2Cl_2 and filtered through a Celite pad. The resulting yellow solution was concentrated to *ca.* 3 mL and ether was added. Cooling the mixture −30 °C gave **13a** as yellow crystals (97 mg, 0.109 mmol, 55% yield). UV-vis (λ_{max}/nm, ε/M^{-1} cm^{-1}): 244 (3.88×10^4), 292 (1.54×10^4), 301 (1.51×10^4), 338 (4.52×10^3), 420 (2.43×10^4), 647 (6.44), 752 (3.02). IR (cm^{-1}; KBr) 2987 (sh), 2942 (m), 2835 (w), 1584 (s), 1512 (m), 1462 (m), 1443 (m), 1374 (w), 1294 (vs), 1168 (s), 1142 (vs, $\nu_{P=O}$), 1112 (s), 1039 (s), 1010 (s), 856 (m), 833 (m), 768 (s), 738 (m), 724 (s), 646 (m), 616 (m), 589 (s, $\delta_{P=O}$). Anal. Calc. for $C_{28}H_{37}N_3O_{12}P_6ClCoNi$ (**13a**·$(CH_2Cl_2)_{0.5}$): C, 37.83; H, 4.19; N, 4.73; Cl, 7.98. Found: C, 37.63; H, 4.20; N, 4.63; Cl, 7.93%.

L_{OMe}Ni(bipy)-OC_6F_5 13b. This complex was prepared according to a similar procedure to the synthesis of **13a** (see above). **13b** (green powder, 45% yield): UV-vis (λ_{max}/nm, ε/M^{-1} cm^{-1}): 242 (3.78×10^4), 292 (1.25×10^4), 301 (1.31×10^4), 332 (3.86×10^3), 655 (7.37), 760 (4.10). IR (cm^{-1}; KBr) 2977 (w), 2946 (m), 2846 (m), 1605 (m), 1495 (vs), 1445 (m), 1173 (sh), 1139 (vs, $\nu_{P=O}$), 1101 (w), 1044 (s), 1006 (s), 975 (sh), 829 (m), 764 (s), 738 (s), 620 (sh), 583 (s, $\delta_{P=O}$). Anal. Calc. for $C_{27}H_{31}N_2O_{10}F_5P_3CoNi$: C, 38.19; H, 3.55. Found: C, 38.15; H, 3.55%.

[L_{OMe}Ni(bipy)(MeCN)]BPh_4 14. Stirring a mixture of **8(Ni)** (227 mg, 0.312 mmol) and $NaBPh_4$ (160 mg, 0.494 mmol) dissolved in MeOH (15 mL) for 5 h at room temperature gave green precipitates, which were collected by filtration on a glass frit and washed with a small amount of MeOH, and dried under reduced pressure. **14** (green crystals, 137 mg, 0.133 mmol, 43% yield): UV-vis (λ_{max}/nm, ε/M^{-1} cm^{-1}; in CH_3CN): 212 (3.84×10^4), 239 (7.39×10^4), 292 (2.21×10^4), 302 (2.20×10^4), 331 (5.42×10^3), 619 (5.5), 740 (sh, 2.5). IR (cm^{-1}; KBr) 3106 (w), 3056 (w), 2985 (w), 2945 (m), 2838 (w), 1600 (m), 1578 (w), 1473 (m), 1445 (s), 1426 (m), 1312 (w), 1251 (w), 1173 (sh), 1136 (vs, $\nu_{P=O}$), 1042 (vs), 1009 (vs), 846 (m), 835 (m), 771 (vs), 729 (s), 705 (s), 653 (w), 612 (sh), 585 (s, $\delta_{P=O}$). Anal. Calc. for $C_{47}H_{54}BN_3O_9P_3CoNi$: C, 55.00; H, 5.30; N, 4.09. Found: C, 54.47; H, 5.38; N, 4.09%.

[L_{OMe}Mn(py)(NO_3)]$_2$ 15. To $Mn(NO_3)_2 \cdot 6H_2O$ (889 mg, 0.310 mmol) dissolved in MeOH (8 mL) was added a MeOH solution (15 mL) of NaL_{OMe} (466 mg, 0.984 mmol) over a period of 2 h and the resultant yellow mixture was stirred for 30 min. The volatiles were removed under reduced pressure and the residue was extracted with CH_2Cl_2 and filtered through a Celite pad. Pyridine (0.15 mL, 1.85 mmol) was added to the filtrate, which was subsequently stirred for 4 h. The mixture was dried under reduced pressure and extracted with toluene (15 mL) and CH_2Cl_2 (2 mL). After removal of the volatiles the residue was crystallized from CH_2Cl_2–ether at −30 °C. **15** (orange yellow crystals, 523 mg, 0.404 mmol, 82% yield): UV-vis (λ_{max}/nm, ε/M^{-1} cm^{-1}): 244 (6.66×10^4), 337 (6.37×10^3). IR (cm^{-1}; KBr) 2981 (sh), 2946 (m), 2842 (w), 1640 (w), 1604 (m), 1474 (s), 1448 (sh), 1385 (vs), 1297 (w), 1142 (vs, $\nu_{P=O}$), 1034 (vs), 1001 (vs), 835 (m), 818 (w), 765 (s), 720 (s), 706 (sh), 589 (s, $\delta_{P=O}$). Anal. Calc. for $C_{32}H_{56}N_2O_{24}P_6Mn_2Co_2$: C, 29.69; H, 4.36; N, 4.33. Found: C, 29.34; H, 4.29; N, 4.38%.

[L_{OMe}Mn(N_3)]$_4$ 3(Mn). NaN_3 (24 mg, 0.32 mmol) was suspended in a CH_2Cl_2 solution (10 mL) of **15** (159 mg, 0.123 mmol) and the mixture was stirred overnight. Filtration through a Celite pad, concentration to *ca.* 5 mL under reduced pressure, addition of ether and cooling at −30 °C gave **3(Mn)** (103 mg, 0.094 mmol, 76% yield) as yellow powder. UV-vis (λ_{max}/nm, ε/M^{-1} cm^{-1}): 245 (1.31×10^5), 339 (1.74×10^4). IR (cm^{-1}; KBr) 2946 (m), 2840 (w), 2080 (vs, ν_{N_3}), 1458 (vs), 1426 (w), 1313 (w), 1246 (w), 1138 (vs, $\nu_{P=O}$), 1100 (w), 1039 (w), 1009 (s), 834 (m), 773 (s), 723 (s), 638 (sh), 587 (s, $\delta_{P=O}$). Anal. Calc. for $C_{44}H_{92}N_{12}O_{36}P_{12}Mn_4Co_4$: C, 24.11; H, 4.23; N, 7.67. Found: C, 23.59; H, 3.84; N, 7.51%.

[L_{OMe}Mn(OC_6H_3-2,6-Me_2)]$_2$ 5b(Mn). To a THF solution (20 mL) of 2,6-dimethylphenol (69 mg, 0.567 mmol) was added excess NaH (45 mg, 1.13 mmol) and the resulting mixture was stirred for 30 min. Then the mixture was filtered through a Celite pad and the filtrate was treated with **15** (348 mg, 0.269 mmol) dissolved in THF (10 mL). Work-up as described for **5b(Ni)** gave **5b(Mn)** (225 mg, 0.179 mmol, 67% yield) as orange crystals. UV-vis (λ_{max}/nm, ε/M^{-1} cm^{-1}): 242 (6.27×10^4), 333 (1.14×10^4). IR (cm^{-1}; KBr) 2946 (m), 2839 (w), 1588 (w), 1468 (m), 1426 (m), 1271 (m), 1233 (m), 1134 (vs, $\nu_{P=O}$), 1089 (w), 1036 (s), 1005 (s), 833 (m), 770 (s), 725 (s), 588 (s, $\delta_{P=O}$). Anal. Calc. for $C_{38}H_{64}O_{20}P_6Mn_2Co_2$: C, 36.38; H, 5.14. Found: C, 35.89; H, 5.08%.

[L_{OMe}Mn(OC_6H_3-2-NO_2)]$_2$ 6c(Mn). This complex was prepared following the procedure described for **5b(Mn)**. **6c(Mn)** (reddish brown crystals, 65% yield): UV-vis (λ_{max}/nm, ε/M^{-1} cm^{-1}): 241 (1.03×10^5), 283 (sh, 4.55×10^4), 330 (2.02×10^4). IR (cm^{-1}; KBr) 2945 (m), 2843 (w), 1600 (m), 1556 (m), 1496 (s), 1346 (s), 1334 (m), 1255 (s), 1133 (vs, $\nu_{P=O}$), 1099 (w), 1030 (s), 1006 (s), 882 (w), 833 (w), 771 (s), 750 (s), 619 (sh), 593 (s, $\delta_{P=O}$). Anal. Calc. for $C_{34}H_{54}N_2O_{24}P_6Mn_2Co_2$: C, 31.70; H, 4.32; N, 2.17. Found: C, 31.60; H, 4.22; N, 2.14%.

[L_{OMe}Mn(bipy)(κ^1-NO_3)] 8(Mn). Upon addition of bipy (46 mg, 0.296 mmol) to a CH_2Cl_2 solution of **15** (187 mg, 0.145 mmol) the yellow solution gradually turned into orange yellow. The resultant mixture was stirred overnight and addition of ether caused precipitation of the product as orange yellow

Table 5 Crystallographic data

Compound	**3(Ni)**·$(CH_2Cl_2)_{4.5}$	**4(Ni)**·THF	**5b(Ni)**·CH_2Cl_2	**5b(Co)**·CH_2Cl_2	**5b(Mn)**·CH_2Cl_2	**6d(Ni)**·$(CH_2Cl_2)_2$	**6e(Ni)**·$(THF)_2$
Formula	$C_{49.50}H_{103}N_{12}O_{36}$-$P_{12}Cl_{11}Co_4Ni_4$	$C_{26}H_{54}O_{19}P_6$-Co_2Ni	$C_{39}H_{66}O_{20}P_6$-$Cl_2Co_2Ni_2$	$C_{39}H_{66}O_{20}P_6$-Cl_2Co_4	$C_{39}H_{66}O_{20}P_6$-$Cl_2Co_2Mn_2$	$C_{38}H_{46}N_2O_{26}$-$P_6Cl_4Co_2Ni_2$	$C_{42}H_{66}O_{24}F_{10}$-$P_6Co_2Ni_2$
Formula weight	2674.6	1033.1	1346.9	1347.4	1339.4	1509.7	1566.1
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$C2/c$	$P2_1/a$	$P2_1/a$	$P2_1/a$	$P\bar{1}$	$P2_1/a$
a/Å	15.391(8)	19.497(8)	19.103(5)	19.005(7)	18.968(3)	14.389(4)	9.2507(14)
b/Å	27.946(5)	11.9703(18)	14.800(2)	14.9328(16)	15.162(8)	18.824(3)	28.276(8)
c/Å	23.403(11)	17.705(7)	21.340(2)	21.355(3)	21.543(5)	14.313(10)	12.140(2)
α/°						112.360(7)	
β/°	91.61(5)	98.32(4)	113.253(3)	113.004(16)	113.058(14)	119.89(3)	100.241(9)
γ/°						88.509(13)	
V/Å^3	10062(7)	4089(2)	5543.4(17)	5579(2)	5701(3)	3043(2)	3124.9(12)
Z	4	4	4	4	4	2	2
μ/cm^{-1}	1.938	1.565	1.594	1.505	1.334	1.556	1.372
No. of data collected	14590	4300	9434	10632	8897	10105	5422
No. of parameters refined	1186	252	716	796	716	831	421
$R1$ for data with $F_o > 4\sigma(F_o)$	0.0888 (11202)	0.0728 (4062)	0.0591 (8690)	0.0760 (10114)	0.0784 (7813)	0.1039 (9276)	0.0894 (5138)
$wR2$ for all data	0.2163 (14590)	0.1974 (4300)	0.1740 (9434)	0.2080 (10632)	0.2146 (8897)	0.2839 (10105)	0.2371 (5422)

Compound	**7c(Ni)**·$(CH_2Cl_2)_2$	**7c(Mn)**	**9(Ni)**	**10**	**13a**·CH_2Cl_2	**14**·OEt_2
Formula	$C_{36}H_{58}N_2O_{24}$-$P_6Cl_4Co_2Ni_2$	$C_{34}H_{54}N_2O_{24}$-$P_6Co_2Mn_2$	$C_{17}H_{39}N_3O_{12}$-P_3CoNi	$C_{21}H_{31}N_5O_9$-P_3CoNi	$C_{28}H_{37}N_3O_{12}$-P_3Cl_2CoNi	$C_{51}H_{64}BN_3O_{10}$-P_3CoNi
Formula weight	1465.8	1288.4	688.1	708.06	889.1	1100.4
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$C2/c$	$P\bar{1}$	$P2_1/c$	$P2_1/a$	$Pbca$	$P2_1/n$
a/Å	24.196(4)	15.558(8)	9.0941(13)	13.959(7)	19.733(3)	12.468(2)
b/Å	24.838(3)	19.023(7)	17.068(3)	11.083(4)	18.21(1)	16.435(3)
c/Å	10.667(2)	8.898(3)	17.876(8)	19.026(3)	20.146(4)	26.532(12)
α/°		97.65(2)				
β/°	100.374(3)	92.10(3)	94.982(5)	109.61(2)		96.85(3)
γ/°		80.74(3)				
V/Å^3	6305.9(17)	2575.5(19)	2764.2(14)	2772.6(17)	7239(6)	5398(3)
Z	4	2	4	4	8	4
μ/cm^{-1}	1.497	1.379	1.516	1.509	1.322	0.802
No. of data collected	5546	6237	5565	5521	6391	9507
No. of parameters refined	349	643	371	362	505	640
$R1$ for data with $F_o > 4\sigma(F_o)$	0.0754 (5164)	0.1332 (4895)	0.0588 (5395)	0.0624 (5238)	0.0764 (5402)	0.0701 (8806)
$wR2$ for all data	0.2172 (5546)	0.3215 (6237)	0.1789 (5565)	0.1737 (5521)	0.1984 (6391)	0.2063 (9507)

solid, which was collected on a glass frit and dried under reduced pressure. **8(Mn)** (84% yield): UV-vis (λ_{max}/nm, ε/M^{-1} cm^{-1}): 241 (1.03×10^5), 243 (5.11×10^4), 288 (sh, 2.21×10^4), 295 (2.21×10^4), 337 (6.32×10^3). IR (cm^{-1}; KBr) 3048 (w), 2947 (m), 2838 (w), 1602 (m), 1596 (m), 1507 (w), 1474 (s), 1441 (s), 1409 (s), 1384 (w), 1314 (s), 1134 (vs, $\nu_{P=O}$), 1097 (w), 1031 (vs), 1010 (vs), 832 (m), 770 (s), 737 (w), 722 (s), 650 (w), 614 (w), 586 (s, $\delta_{P=O}$), 577 (s). Anal. Calc. for $C_{21}H_{13}N_3O_{12}P_3MnCo$: C, 34.58; H, 4.31; N, 5.80. Found: C, 34.82; H, 4.21; N, 6.30%.

X-Ray crystallography

Single crystals of **3(Ni)** (CH_2Cl_2), **4(Ni)** (THF), **5b(Ni)** (CH_2Cl_2–ether), **5b(Co)** (CH_2Cl_2–ether), **5b(Mn)** (CH_2Cl_2–ether), **6e(Ni)** (THF–ether), **6d(Ni)** (CH_2Cl_2–ether), **7c(Ni)** (CH_2Cl_2–ether), **7c(Mn)** (CH_2Cl_2–ether), **9(Ni)** (CH_2Cl_2–ether), **10** (MeOH–ether), **13a** (CH_2Cl_2–ether), and **14(Ni)** (MeCN–ether) were obtained by recrystallization from the solvent systems shown in the parentheses and mounted on glass fibers.

Diffraction measurements were made on a Rigaku RAXIS IV imaging plate area detector with Mo-Kα radiation ($\lambda = 0.71069$ Å) at −60 °C. In the reduction of data, Lorentz and polarization corrections and empirical absorption corrections[13] were made. Crystallographic data and results of structure refinements are listed in Table 5, and details of measurements and refinements were similar to those in ref. 5. Least-squares refinements (refined on F^2) were carried out using SHELXL 93[13a] (**9(Ni)** and **10**) or SHELXL 97[13b] (the others). Unless otherwise stated non-hydrogen atoms were refined with anisotropic thermal parameters.

Two independent molecules were included in unit cells of **6d(Ni)** and **7c(Mn)**. Disordered structures were as follows and refined taking into account two components: **5b(Ni)**, **5b(Mn)**: 2,6-dimethylphenyl parts (C91–C108 : C111–C128 (refined isotropically) = 0.61 : 0.39) were found to be disordered. **5b(Co)**: 2,6-dimethylphenyl parts (C91–C108 : C111–C128 = 0.60 : 0.40). **6d(Ni)**: MeO oxygen atoms (O12–O33 : O12A–O33A = 0.535 : 0.465; O72–O93 : O72A–O93A = 0.538 : 0.462). **6e(Ni)**: THF solvate (O61–C64–C63 : O61A–C64A–C63A: 0.58 : 0.42). **9(Ni)**: NO_3 oxygen atoms (O1–O3 : O1A–O3A = 0.679 : 0.321). **10**: Cp ring (C41–C45 : C41A–C45A = 0.6 : 0.4). **13a**: OMe oxygen atoms (O11–O33 (refined isotropically) : O11a–O33a (refined isotropically) = 0.52 : 0.48). Complex **7c(Mn)** has a high R factor compared to the other samples due to the small number of data and the small size of crystals of lower quality.

CCDC reference number 186/1842.

See http://www.rsc.org/suppdata/dt/a9/a909580b/ for crystallographic files in .cif format.

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