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Synthesis and Structure of Allyl and Alkynyl Complexes of Manganese(II) Supported by a Bulky β-Diketiminate Ligand†

Jianfang Chai, Hongping Zhu, Herbert W. Roesky,* Zhi Yang, Vojtech Jancik,
Regine Herbst-Irmer, Hans-Georg Schmidt, and Mathias Noltemeyer

Institut für Anorganische Chemie der Universität Göttingen,
Tammannstrasse 4, D-37077 Göttingen, Germany

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Reaction of LK (L = HC(CMeNAr)$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$) and MnCl$_2$(THF)$_{1.5}$ in THF unexpectedly resulted in the formation of the trinuclear complex LMn(μ-Cl)$_2$Mn(THF)$_2$(μ-Cl)$_2$MnL (**1**) in good yield. The substitution reactions of **1** with C$_3$H$_5$MgCl and PhCCLi, respectively, provided the monomeric LMnC$_3$H$_5$(THF) (**2**) and the dimeric [LMn(μ-CCPh)]$_2$ (**3**) in moderate yield. Complexes **1**−**3** were characterized by single-crystal X-ray structural analysis. The structures show that compound **1** contains an ideal planar Mn$_3$Cl$_4$ core and a linear Mn$_3$ trimer, the allyl ligand in **2** is in an η^1 mode, and there is π-interaction between the triple bond and the metal center in **3**.

Introduction

Allyl and alkynyl complexes of transition metals are important due to their synthetic methodology, theoretical implications, and the advantage of applications in organic synthesis and catalysis.[1] In addition, allyl and alkynyl complexes are of particular interest owing to the versatile bonding mode of the allyl and alkynyl groups to metal centers, which can be either σ-bonded or π-bonded.[1e,2] Besides the traditional interest in organometallic chemistry, metal-alkynyl complexes have recently attracted special attention regarding their potential in material science applications.[3] The extended −C≡C− unit and its potential to act as a ‘molecular wire’ resulted in interesting electronic and structural properties of the materials containing alkynyl groups.[3]

In the past few years there is increasing interest in the β-diketiminate ligands, especially in those with bulky aryl groups at the nitrogen, which have excellent steric and electronic properties to stabilize unusual coordination sites.[4] A variety of main group element, transition metal, and lanthanide complexes containing such ligands have been synthesized and characterized, some of which have novel structures and excellent catalytic activities.[4] For example, the first monomeric Al(I) compound of composition LAl was synthesized (L = HC(CMeNAr)$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$) as a stable carbene analogue.[5] Very recently we reported on the synthesis and structure of the aluminum dihydroxide with terminal OH groups and the first terminal hydroxide containing alumoxane using the same ligand.[6] Despite the impressive results obtained so far, the utilization of such ligand systems in the synthesis of allyl and alkynyl complexes still remains rare. To the best of our knowledge, only few such complexes including {HC(CtBuNAr)$_2$}MgC$_3$H$_5$(THF),[7] [{HC(CtBuNAr)$_2$}Mg(μ-C$_3$H$_5$)]$_6$,[7] {HC(CMeNAr′)$_2$}B(C$_3$H$_5$)$_2$[8] (Ar′ = 4-MeC$_6$H$_4$), and LZnCCPh[9] are reported. After the interesting results were obtained with main group elements by taking advantage of the β-diketiminate ligands,[4,5,10] we became interested in transition metals and investigated the synthesis and reactivity of organomanganese complexes supported by such ligands. A series of manganese(II) complexes including the alkyl and aryl derivatives [LMn(μ-Me)]$_2$ and LMnPh have been synthesized

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† Dedicated to Professor Manfred Meisel on the occasion of his 65th birthday.

* To whom correspondence should be addressed. E-mail: hroesky@gwdg.de.

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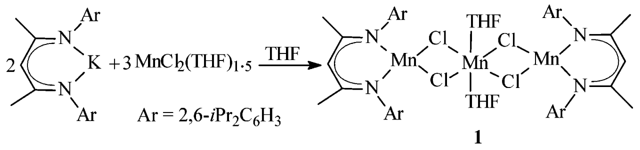
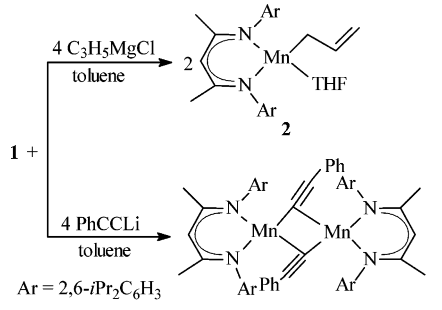
10.1021/om049605k CCC: $27.50

Scheme 1



Scheme 2



and well characterized.[11] Herein we report on the synthesis and structure of the trimeric complex LMn(μ-Cl)$_2$Mn(THF)$_2$(μ-Cl)$_2$MnL (**1**) containing the same bulky β-diketiminate ligand and its allyl and alkynyl derivatives LMnC$_3$H$_5$(THF) (**2**) and [LMn(μ-CCPh)]$_2$ (**3**).

Results and Discussion

Synthesis of Compounds 1−3. We have reported the reaction of LK (L = HC(CMeNAr)$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$) and MnCl$_2$ in diethyl ether to afford the dimeric complex [LMn(μ-Cl)]$_2$.[11c] However, the similar reaction of LK and MnCl$_2$(THF)$_{1.5}$ in THF unexpectedly resulted in the formation of the trimer LMn(μ-Cl)$_2$Mn(THF)$_2$(μ-Cl)$_2$MnL (**1**) in good yield, although a ratio of 1: 1 of the starting materials was employed (Scheme 1).

The addition of C$_3$H$_5$MgCl and PhCCLi, respectively, to **1** in toluene at low temperature smoothly provided the monomeric compound LMnC$_3$H$_5$(THF) (**2**) and the dimer [LMn(μ-CCPh)]$_2$ (**3**) in moderate yield (Scheme 2). The efforts to identify other species were unsuccessful. Compared with the metathesis reaction of the dimers [LMn(μ-Cl)]$_2$ and [LMn(μ-I)]$_2$ with MeLi and PhLi,[11] the reactions of **1** with C$_3$H$_5$MgCl and PhCCLi resulted in *easily available products that can be purified by recrystallization.*

Complexes **1**−**3** are yellow crystalline solids and soluble in THF. Compounds **2** and **3** are sensitive to air and moisture and have a much better solubility than **1**. These complexes were characterized by elemental analyses, EI-MS, and IR. EI-MS of **1** shows that the molecular ion peak is silent; rather, [LMnCl]$^+$ is observed as the most intense ion at *m*/*z* 507. In the EI-MS of **2**, [LMnC$_3$H$_5$]$^+$ appears at *m*/*z* 537 (8%) without the coordinated THF, followed by *m*/*z* 472 [LMn]$^+$ as the most intense peak. Interestingly, the molecular ion [M]$^+$ at *m*/*z* 1146 in the mass spectrum of **3** can be seen albeit with very low intensity (1%), followed by [1/2M]$^+$ *m*/*z* 573 (40%) and [LMn − H]$^+$ *m*/*z* 471 (100%). The vibration for the bridging −C≡C− group in the IR spectrum of **3** appears at 2034 cm^{-1}, which is consistent with the decrease of the bond strength of the C≡C unit due to the π-interaction with the metal center.

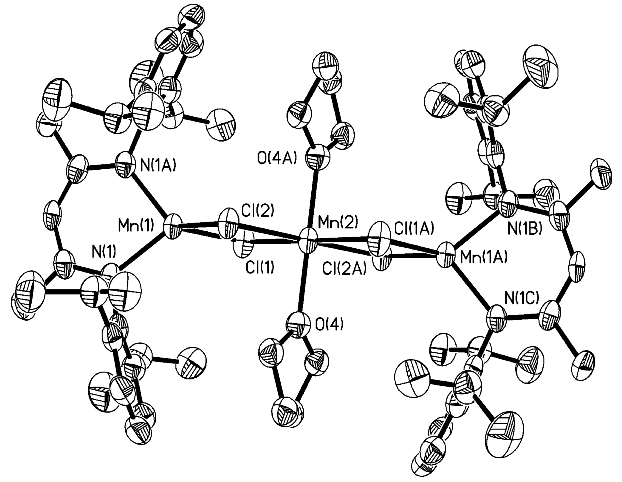


Figure 1. Molecular structure of **1** (50% probability thermal ellipsoids). Hydrogen atoms are omitted for clarity.

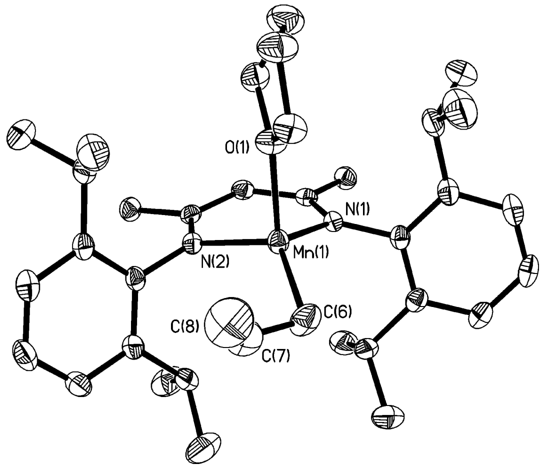


Figure 2. Molecular structure of **2** (50% probability thermal ellipsoids). Hydrogen atoms are omitted for clarity.

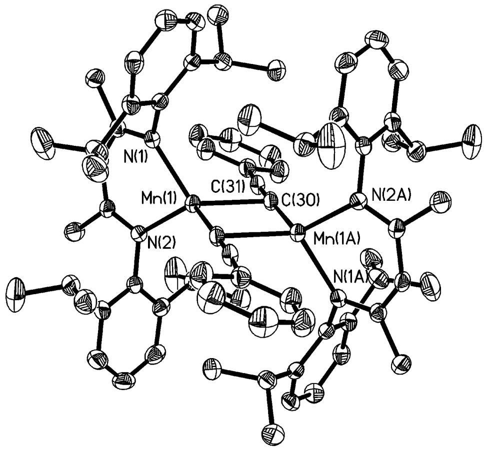


Figure 3. Molecular structure of **3** (50% probability thermal ellipsoids). Hydrogen atoms are omitted for clarity.

X-ray Solid-State Structural Analysis. Complexes **1**−**3** were characterized by single-crystal X-ray diffraction. The structures of **1**−**3** are shown in Figures 1−3, respectively. Crystallographic data are given in Table 1, and selected bond lengths and angles in Table 2.

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Table 1. Crystallographic Data for Complexes 1−3

	1 incl. 4 THF	**2**	$^1/_2$ **3**
formula	$C_{82}H_{130}Cl_4Mn_3N_4O_6$	$C_{36}H_{54}MnN_2O$	$C_{37}H_{46}MnN_2$
fw	1574.52	585.75	573.70
T (K)	133(2)	133(2)	100(2)
λ (Å)	0.71073	0.71073	1.54178
cryst syst	monoclinic	triclinic	monoclinic
space group	$C2/m$	$P\bar{1}$	$P2(1)/n$
a (Å)	17.238(3)	9.034(2)	14.010(1)
b (Å)	18.411(3)	12.177(4)	13.257(1)
c (Å)	14.729(2)	15.95(2)	17.697(1)
α (deg)	90.00	87.22(2)	90.00
β (deg)	113.947(13)	77.909(16)	98.59(1)
γ (deg)	90.00	89.24(2)	90.00
V (Å^3)	4272.3(12)	1713.9(7)	3250(1)
Z	2	2	4
D_{calcd} (g cm^{-3})	1.224	1.135	1.172
μ (mm^{-1})	0.612	0.413	3.483
F(000)	1682	634	1228
cryst size (mm^3)	0.30 × 0.20 × 0.20	0.30 × 0.30 × 0.30	0.30 × 0.20 × 0.10
2θ range (deg)	3.02−49.60	3.34−49.44	7.52−118.92
no. of rflns collected	22 430	18 432	15 989
no. of indep rflns	3785 (R(int) = 0.1105)	5810 (R(int) = 0.0417)	4673 (R(int) = 0.0458)
no. of data/restraints/params	3785/0/214	5810/0/379	4673/0/375
goodness-of-fit, F^2	1.028	1.036	1.049
R1, wR2 [$I > 2\sigma(I)$]	0.0777, 0.2045	0.0341, 0.0772	0.0356, 0.0803
R1, wR2 (all data)	0.1171, 0.2295	0.0487, 0.0814	0.0503, 0.0860
largest diff peak/hole (e Å^{-3})	1.021/−0.646	0.380/−0.220	0.441/−0.251

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for Compounds 1−3

Compound **1**			
Mn(1)−N(1)	2.077(5)	N(1)−Mn(1)−N(1A)	91.3(2)
Mn(1)−N(1A)	2.077(4)	N(1)−Mn(1)−Cl(1)	120.65(13)
Mn(1)−Cl(1)	2.391(2)	N(1)−Mn(1)−Cl(2)	117.80(12)
Mn(1)−Cl(2)	2.412(2)	Cl(1)−Mn(1)−Cl(2)	91.36(7)
Mn(2)−Cl(1)	2.576(2)	O(4)−Mn(2)−O(4A)	180.0
Mn(2)−Cl(2)	2.527(2)	O(4)−Mn(2)−Cl(2)	90.0
Mn(2)−O(4)	2.200(6)	O(4)−Mn(2)−Cl(1)	90.0
Mn(1)−Mn(2)	3.564	Cl(1)−Mn(2)−Cl(2)	84.65(6)
Compound **2**			
Mn(1)−N(1)	2.092(2)	N(1)−Mn(1)−N(2)	92.19(6)
Mn(1)−N(2)	2.095(2)	N(1)−Mn(1)−C(6)	123.58(7)
Mn(1)−C(6)	2.132(2)	N(2)−Mn(1)−C(6)	123.35(8)
Mn(1)−O(1)	2.163(1)	N(1)−Mn(1)−O(1)	102.62(6)
C(7)−C(8)	1.305(4)	N(2)−Mn(1)−O(1)	101.77(6)
C(6)−C(7)	1.444(3)	C(6)−Mn(1)−O(1)	109.60(8)
Compound **3**			
Mn(1)−N(1)	2.091(2)	N(1)−Mn(1)−N(2)	89.60(7)
Mn(1)−N(2)	2.105(2)	N(1)−Mn(1)−C(30)	119.51(8)
Mn(1)−C(30)	2.298(2)	N(2)−Mn(1)−C(30)	120.78(7)
Mn(1)−C(30A)	2.133(2)	C(30)−Mn(1)−C(30A)	90.55(8)
Mn(1A)−C(30)	2.133(2)	N(1)−Mn(1)−C(30A)	116.68(8)
Mn(1)−Mn(1A)	3.120(1)	N(2)−Mn(1)−C(30A)	122.72(8)
C(30)−C(31)	1.226(3)	Mn(1A)−C(30)−C(31)	177.17(2)

Compound **1** crystallizes in the monoclinic space group $C2/m$ with two molecules per unit cell. The molecule consists of a linear trimer with four bridging chlorine atoms and two chelating ligands adopting a symmetric structure, which, in fact, is one $MnCl_2(THF)_2$ molecule captured by the $[LMn(\mu\text{-}Cl)]_2$ dimer. The central Mn(2) atom has a distorted octahedral coordination sphere with two THF molecules in *trans* position, while the two remaining manganese atoms achieve a distorted tetrahedral geometry. The internal Cl(1)−Mn(2)−Cl(2) and Mn−Cl−Mn angles (84.7° and av 92.0°, respectively) result in the Mn−Mn distances (3.56 Å), which are longer than the distance (3.28 Å) observed in $[LMn(\mu\text{-}Cl)]_2$.[11c] The two bridging Mn_2Cl_2 rings are ideally coplanar, which bisect and are perpendicular (90.0°) to the two chelating ligands around them. The Mn−N bond lengths compare well with those in $[LMn(\mu\text{-}Cl)]_2$, while the bridging Mn−Cl distances are about 0.07 Å longer.[11c]

Compound **2** is a monomeric species in which the allyl ligand is bound to the four coordinate manganese center in an η^1 arrangement. *To the best of our knowledge,* ***2*** *is the first structurally characterized allyl-manganese complex in an* η^1 *mode of the ligand*. The metal center is of distorted tetrahedral geometry surrounded by the allyl group, a THF molecule, and the chelating ligand. The backbone of the chelating ligand is nearly planar, and the manganese atom is out of this plane (0.53 Å), which is nearly in orthogonal position with the plane formed by Mn(1), C(6), and O(1). The Mn−C bond length (2.13 Å) is in the normal range of the Mn−C single bond and a little shorter than those in manganese complexes with allyl groups in η^3 mode.[12] The large difference between the distances of C(7)−C(8) (1.31 Å) and C(6)−C(7) (1.44 Å) shows that there is no obvious delocalization of π-electrons of the allyl group. The distance between Mn(1) and C(8) (3.88 Å) does not support any bonding interaction. Interestingly, both the N−Mn−N angle (92.2°) and the Mn−N bond lengths (av 2.09 Å) in **2** are larger than the corresponding ones in **1** (91.3° and 2.08 Å, respectively) due to the different *trans* effect.

The solid-state structure of **3** (Figure 3) reveals a dimer formed by two bridging phenylethynyl groups, which is best described by assuming that Mn(1)−C(30) is a σ-bond and that the two monomer units are linked together through π-bonding by donation of π-electron density of one C≡C bond to the empty orbital of the other metal center. To the best of our knowledge, compound **3** is the first structurally characterized dinuclear manganese complex containing bridging alkynyl groups. Similar to complexes **1** and **2**, the manganese atom is out of the chelating ligand plane (0.47 Å). The central core contains an ideal planar four-

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membered Mn_2C_2 ring, which bisects and is perpendicular (90.8°) to the two chelating ligands around it. The distance between the two manganese atoms (3.12 Å) is beyond a Mn−Mn bonding range and is significantly longer than those in dimeric manganese alkyl complexes $[LMn(\mu\text{-Me})]_2$[11b] (2.81 Å) and $[Mn(CH_2SiMe_3)(PMe_3)(\mu\text{-}CH_2SiMe_3)]_2$[13] (2.77 Å). This indicates that the bridge bonding in **3** is different from those in other dimeric species. The carbon−carbon triple bond length (1.23 Å) is longer than the accepted average value of 1.21 Å, reflecting the π-interaction between the triple bond and the metal center. Similar bond lengths are observed in $[CuCl(\eta^2\text{-}PhCCMn(CO)_3(dppe))]$[14] (1.23 Å) and $\{Cu[\eta^2\text{-}t\text{BuCCMn(CO)}_3(dppe)]_2\}PF_6$[1f] (1.24 Å) having alkynyl-manganese groups π-bonded to the copper. Despite the π-interaction between the triple bond and the metal center in **3**, the Mn(1A)−C(30)−C(31) unit remains almost linear (177.0°). The Mn−C bond lengths (av 2.22 Å) are significantly longer than those (1.90−2.08 Å) in manganese complexes with terminal alkynyl groups.[15]

Conclusion

In summary, the trimeric compound $LMn(\mu\text{-Cl})_2Mn(THF)_2(\mu\text{-Cl})_2MnL$ (**1**) (L = $HC(CMeNAr)_2$, Ar = 2,6-$i\text{Pr}_2C_6H_3$) was obtained from the reaction of LK and $MnCl_2(THF)_{1.5}$ when THF was employed as solvent. The substitution reactions of **1** with C_3H_5MgCl and PhCCLi afforded the monomeric η^1-allyl compound **2** and the dimeric alkynyl compound **3**, respectively. The successful isolation of complexes **2** and **3** proves again that β-diketiminate ligands are ideal to prepare organomanganese complexes.

Experimental Section

General Procedures. All reactions were performed using standard Schlenk and drybox techniques. Solvents were appropriately dried and distilled under dinitrogen prior to use. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. Mass spectra were obtained on a Finnigan Mat 8230 instrument. IR spectra were recorded on a Bio-Rad Digilab FTS-7 spectrometer as Nujol mulls between KBr plates. LK[11a] (L = $HC(CMeNAr)_2$, Ar = 2,6-$i\text{Pr}_2C_6H_3$) and $MnCl_2(THF)_{1.5}$[16] were synthesized as described in the literature.

$LMn(\mu\text{-Cl})_2Mn(THF)_2(\mu\text{-Cl})_2MnL$ (1). LK (0.91 g, 2 mmol) in THF (15 mL) was added to a suspension of $MnCl_2(THF)_{1.5}$ (0.70 g, 3 mmol) in THF (40 mL) at −78 °C. The mixture was warmed to room temperature and stirred for 14 h. The precipitate was removed by filtration. The solution was concentrated to ca. 10 mL and kept at 4 °C for 24 h to give yellow crystals. The crystals were collected by filtration, and the mother liquid was concentrated to ca. 5 mL and kept at −26 °C for 24 h to give additional crystals. Total yield: 1.28 g (81%). Mp: >400 °C. Anal. Calcd for $C_{66}H_{98}Cl_4Mn_3N_4O_2$ (1286.51): C, 61.56; H, 7.62; N, 4.35. Found: C, 61.55; H, 7.49; N, 4.21. EI-MS: *m/z* (%) 507 (100) $[LMnCl]^+$. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 1525 (m), 1400 (w), 1316 (s), 1292 (w), 1263 (s), 1230 (w), 1176 (w), 1100 (s), 1098 (m), 1075 (m), 1056 (m), 1022 (s), 934 (w), 852 (w), 794 (s), 758 (m), 721 (w), 636 (w), 527 (w), 468 (w), 452 (w).

$LMnC_3H_5(THF)$ (2). C_3H_5MgCl (1.1 mL, 2.0 M in THF, 2.2 mmol) was added to a suspension of **1** (0.64 g, 0.5 mmol) in toluene (20 mL) at −78 °C. The mixture was allowed to warm to room temperature and stirred for 14 h. All volatiles were removed in a vacuum, and the residue was extracted with hexane (2 × 15 mL). The yellow solution was concentrated to ca. 15 mL and kept at 4 °C for 48 h to give yellow crystals. No other species was isolated. The crystals were collected by filtration, and the filtrate was concentrated and kept at −26 °C for 7 days to give additional crystals. Total yield: 0.25 g (43%). Mp: >173 °C (dec). Anal. Calcd for $C_{36}H_{54}MnN_2O$ (585.75): C, 73.75; H, 9.22; N, 4.78. Found: C, 74.13; H, 8.96; N, 4.64. EI-MS: *m/z* (%) 513 (8) $[M - THF]^+$, 472 (100) $[LMn]^+$. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 1653 (w), 1521 (m), 1401 (m), 1317 (m), 1262 (s), 1175 (w), 1098 (s), 1021 (m), 933 (w), 847 (w), 794 (m), 760 (w), 738 (w), 722 (m), 693 (w), 663 (w).

$[LMn(\mu\text{-CCPh})]_2$ (3). PhCCLi (2.2 mL, 1.0 M in THF, 2.2 mmol) was added to a suspension of **1** (0.64 g, 0.5 mmol) in toluene (20 mL) at −78 °C. The mixture was allowed to warm to room temperature and stirred for 14 h. All volatiles were removed in a vacuum, and the residue was extracted with hexane (2 × 15 mL). The yellow solution was concentrated to ca. 15 mL and kept at 4 °C for 48 h to give yellow crystals. No other species was isolated. The crystals were collected by filtration, and the filtrate was concentrated and kept at −26 °C for 4 days to give additional crystals. Total yield: 0.32 g (56%). Mp: >170 °C (dec). Anal. Calcd for $C_{74}H_{92}Mn_2N_4$ (1147.4): C, 77.39; H, 8.02; N, 4.88. Found: C, 77.13; H, 8.46; N, 4.72. EI-MS: *m/z* (%) 1146 (1) $[M]^+$, 573 (40) $[1/2M]^+$, 471 (100) $[LMn - H]^+$. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 2034 (w), 1524 (m), 1317 (m), 1260 (s), 1177 (w), 1098 (s), 1056 (m), 1021 (s), 931 (w), 865 (w), 756 (w), 721 (m).

X-ray Crystallography. Crystallographic data for **1** and **2** were collected on a Stoe IPDS II-array detector system with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and for **3** on a Bruker three-circle diffractometer equipped with a SMART 6000 CCD detector using Cu Kα radiation (λ = 1.54178 Å). All structures were solved by direct methods (SHELXS-97)[17] and refined against F^2 using SHELXL-97.[18] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included at geometrically calculated positions and refined using a riding model.

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Supporting Information Available: X-ray structural information for complexes **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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