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Syntheses of novel di- and trinucleating ligands having a triethylbenzene core with N,N-bidentate tethers: their complexation toward Pd and Rh organometallic fragments†

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A series of di- and trinucleating ligands with a 1,3,5-triethylbenzene core connected to N,N-bidentate tethers was synthesized. The ligands readily reacted with monuclear Rh and Pd precursors to give the corresponding di- and trinuclear complexes, which were characterized by using NMR and ESI mass spectroscopy. In the solid state, the trinuclear complexes with ligands having pyridylpyrazolyl tethers adopt the most stable *ababab* configuration, in which the organometallic fragments are on the same side of the benzene plane. On the other hand, in solution, the linker moieties between the benzene core and the metals are flexible enough to interconvert between other configurations, that is, they exhibit dynamic behavior, and the rotational barrier was dependent on the length of the linkers. From variable temperature (VT) ^{1}H NMR measurements, the rotational barrier for a trinuclear Rh–CO complex with a ligand having methylene linkers was estimated to be ~12.6 kcal mol^{-1}. However, no spectral changes were observed for the ethylene derivative in the temperature range of −60 °C to 50 °C, indicating that the rotation was not frozen out on the ^{1}H NMR timescale, even at −60 °C.

Introduction

Controlling the structure of multinuclear complexes with the appropriate supporting ligands has brought about a variety of unique reactions.[1] It has been shown that the reaction site provided by the complexes plays a key role in the activation of substrates through cooperative interaction of the metal centers.[2] Until now, much of the research on multinuclear organometallic complexes has involved clusters with metal–metal bonds, and little attention has been paid to clusters with no metal–metal bonds.[2] However, model systems of metalloenzymes with well-designed multidentate ligands have been extensively studied.[3] To gain a better understanding of clusters without metal–metal bonds, we have been studying multinuclear complexes with 3,5-bis((diphenylphosphino)methyl)pyrazolato (PNNP)[4] and (3-(diphenylphosphino)methyl-5-pyridylpyrazolato (PNNN) ligands, which separate the metal centers beyond the distance for metal–metal bonding interaction but are flexible enough to accommodate substrates of various sizes.[5] With the aim of extending our study to multinuclear complexes without metal–metal bonds, we started investigating complexes having a ligand with a 1,3,5-triethylbenzene core, which can arrange the metal centers to form a three-dimensional coordination site. Thus far, to the best of our knowledge, there are no examples of a multinuclear complex having a 1,3,5-triethylbenzene core and reactive organometallic fragments. Recently, 1,3,5-triethylbenzene derivatives with functionalized pendant arms have been widely used as a core in molecular recognition[6] and biomimetic[7] and supramolecular chemistry.[8] The 1,3,5-triethylbenzene derivatives effectively force the tethers at the 2, 4 and 6 positions to be on the same side of the phenyl ring, meaning that the ligand adopts an *ababab* (*a* denotes 'above' and *b* denotes 'below') configuration. The *ababab* configuration is thermodynamically the most stable configuration, because the steric repulsion between the adjacent substituents is minimized (Fig. 1). This configuration makes it possible to introduce metal centers at the 2, 4 and 6 positions, indicated by "functional group" in Fig. 1, thus forming a multinuclear reaction site in which organic substrates can be activated in a concerted manner. Here, we report the syntheses of di- and trinucleating ligands having a 1,3,5-triethylbenzene core and their complexes with Pd and Rh organometallic fragments. Properties of the ligands having different chain lengths between the core phenyl ring and the N,N-bidentate coordination site and their complexes are compared. Conformational flexibility and reactivity studies of the new multinuclear complexes are also described.

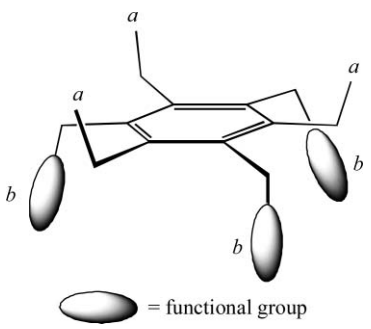

Fig. 1 Steric configuration of the substituents of 1,3,5-triethylbenzene derivatives.

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† Electronic supplementary information (ESI) available: Crystallographic results; crystallographic data in CIF format (CCDC reference numbers 659502–659504). See DOI: 10.1039/b713503c

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Results and discussion

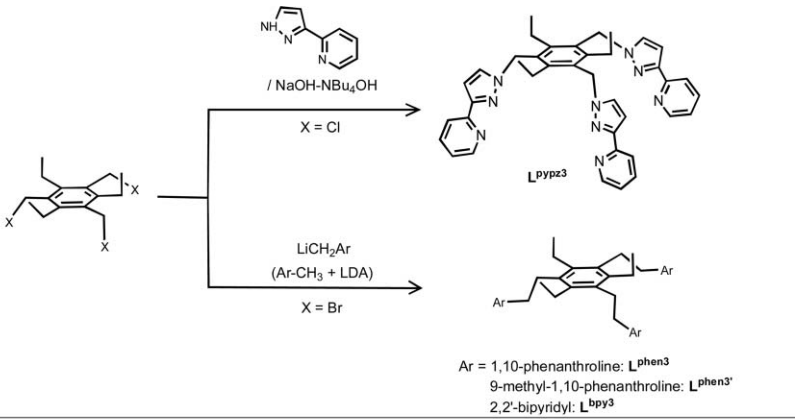
Ligand synthesis

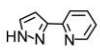
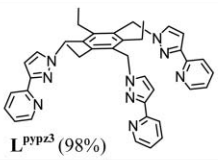
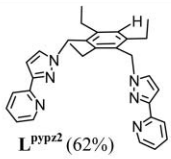
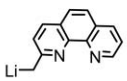
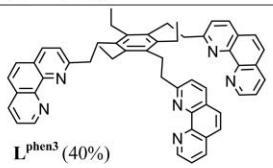
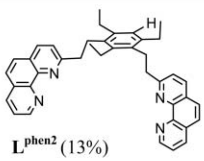
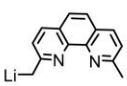
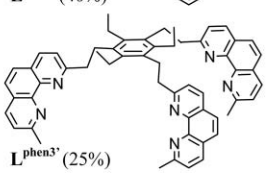
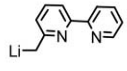
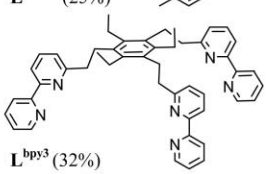
Scheme 1 shows the synthetic routes used to prepare the trinucleating ligands $\mathbf{L}^{pypz3}$, $\mathbf{L}^{phen3}$, $\mathbf{L}^{phen3'}$ and $\mathbf{L}^{bpy3}$, which have different alkyl chain lengths between the benzene core and the N,N-bidentate coordination site. The corresponding dinucleating ligands $\mathbf{L}^{pypz2}$ and $\mathbf{L}^{phen2}$ were also synthesized for comparison. All of the ligands were synthesized *via* a nucleophilic substitution reaction involving 1,3,5-tri(halomethyl)- or 1,3-di(halomethyl)-2,4,6-triethylbenzene[9] and the appropriate nucleophile (Scheme 1).

The 3-(2-pyridyl)pyrazolyl derivatives with methylene linkers, $\mathbf{L}^{pypz3}$ and $\mathbf{L}^{pypz2}$, were prepared by reacting the appropriate 2,4,6-triethylbenzene starting material with 3-(2-pyridyl)pyrazole under phase transfer conditions (NaOH in H_2O–toluene–40% NBu_4OH). The 1,10-phenanthroline (phen) and 2,2′-bipyridyl (bpy) derivatives with ethylene linkers were prepared by reacting with a carbanion species generated by deprotonation of the corresponding methyl derivatives with lithium diisopropylamide (LDA). The yields were lower than those of the pyridylpyrazolyl (pypz) ligands, probably due to the instability of the carbanion species.

Synthesis of di- and trinuclear complexes

The obtained polynucleating ligands were converted to polynuclear organometallic species (**1**, **2**, **8**, and **9** with 3-(2-pyridyl)-pyrazolylmethyl tethers; **4**, **5**, **6**, **11**, and **12** with the phenanthrylethyl tethers) by treating with labile Pd ([(cod)Pd(η^3-C_3H_5)]BF_4, (cod)PdMeCl) and Rh precursors ([Rh(cod)$_2$]BF_4, [Rh(nbd)$_2$]BF_4 (cod = 1,5-cyclooctadiene; nbd = 2,5-norbornadiene)), and the results are summarized in Schemes 2 and 3. Rh–diene complexes **2**, **6**, and **9** were carbonylated under an atmospheric pressure of CO to give the corresponding Rh–CO complexes **3**, **7**, and **10**, respectively. The Pd–Cl complex formed in the reaction of $\mathbf{L}^{phen3}$ and (cod)PdMeCl was converted to the MeCN-coordinated cationic species **5** by abstracting Cl^- with AgOTf in MeCN. Attempts to isolate analytically pure trinuclear complexes with $\mathbf{L}^{bpy3}$ were unsuccessful due to the high solubility of the product.



Linker	Nucleophile	Ligand	
-CH_2-		 $\mathbf{L}^{pypz3}$ (98%)	 $\mathbf{L}^{pypz2}$ (62%)
-CH_2CH_2-		 $\mathbf{L}^{phen3}$ (40%)	 $\mathbf{L}^{phen2}$ (13%)
		 $\mathbf{L}^{phen3'}$ (25%)	
		 $\mathbf{L}^{bpy3}$ (32%)	

Scheme 1

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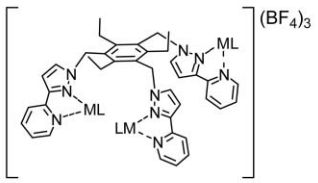
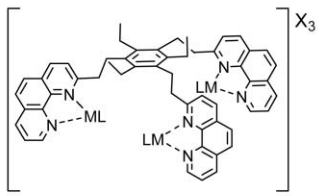
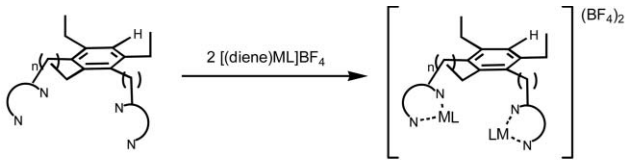
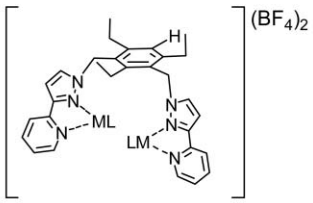
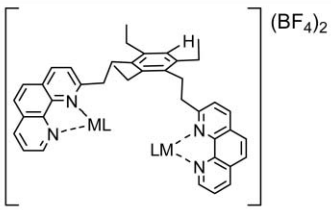
Linker	Ligand	Metal Complex	ML, Yield
-CH_2- (n = 1)	$\mathbf{L}^{pypz3}$		$Pd(C_3H_5)$ (**1**) (70%) Rh(cod) (**2**) (92%) $Rh(CO)_2$ (**3**) (80%)
-CH_2CH_2- (n = 2)	$\mathbf{L}^{phen3}$		$Pd(C_3H_5)$ (**4**) (45%), X = BF_4 PdMe(MeCN) (**5**) (67%), X = OTf Rh(nbd) (**6**) (55%), X = BF_4 $Rh(CO)_2$ (**7**) (83%), X = BF_4

Scheme 2



Linker	Ligand	Metal Complex	ML, Yield
-CH_2- (n = 1)	$\mathbf{L}^{pypz2}$		$Pd(C_3H_5)$ (**8**) (58%) Rh(cod) (**9**) (90%) $Rh(CO)_2$ (**10**) (75%)
-CH_2CH_2- (n = 2)	$\mathbf{L}^{phen2}$		$Pd(C_3H_5)$ (**11**) (40%) Rh(nbd) (**12**) (47%)

Scheme 3

Spectroscopic characterization

All ligands and metal complexes were fully characterized by using ^{1}H and ^{13}C NMR spectroscopy, FAB and ESI mass spectroscopy, respectively, and X-ray structural studies (*vide infra*). The ^{1}H NMR spectrum of the trinucleating ligand $\mathbf{L}^{pypz3}$ measured at room temperature contained only a single set of the resonances for the ethyl, methylene (C_{phenyl}-CH_2-), and pypz parts, which agrees with the pseudo-C_3 symmetry of the molecule (Fig. 2). In the ^{1}H NMR spectrum of the dinucleating ligand $\mathbf{L}^{pypz2}$ with pseudo-C_s symmetry, two sets of inequivalent resonances for the ethyl groups in a 1 : 2 integral ratio were observed, whereas the resonances for the pypz ligand and methylene (C_{phenyl}-CH_2-) protons appeared as a single set of resonances. The signal for H17 on the phenyl ring presumably overlaps that for H12, based on the integral ratio of the signals (Fig. 2). The molecular structure of $\mathbf{L}^{pypz3}$ was determined by using X-ray crystallography.

The NMR spectra of the ethylene-bridged ligands $\mathbf{L}^{phen3}$, $\mathbf{L}^{phen3\prime}$, and $\mathbf{L}^{phen2}$ have spectral features similar to those of the pypz derivatives, which is consistent with the symmetry of the ligands.

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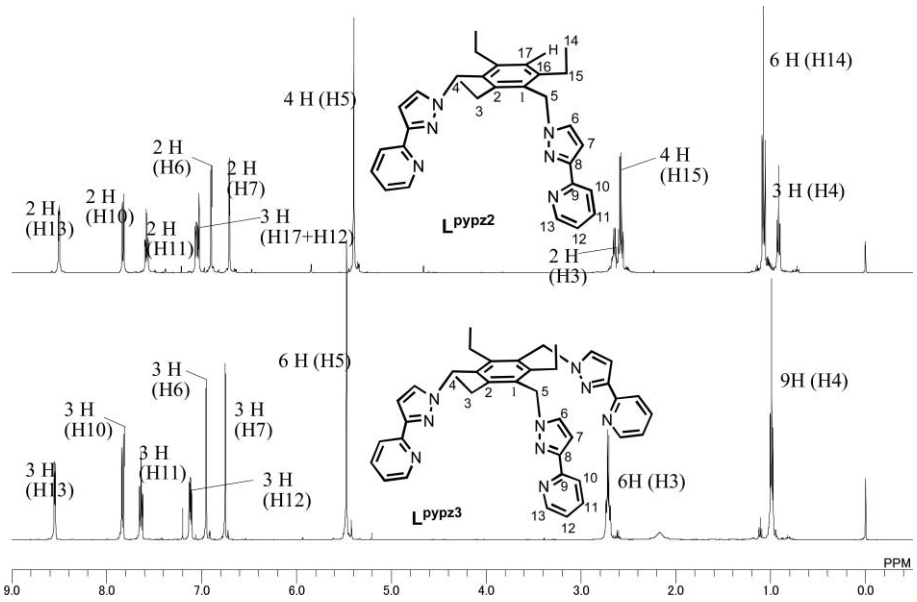

Fig. 2 ^{1}H NMR spectra of $\mathbf{L}^{pypz2}$ and $\mathbf{L}^{pypz3}$.

No spectral changes in the spectra of the ligands were observed in the temperature range of −60 to 50 °C.

Formation of polynuclear complexes **1–7** was evidenced by the downfield shifts of the signals for the olefinic moieties of the diene ligands and the hydrogen atoms adjacent to the coordinated N atom of the tether moieties (*e.g.*, H18 for $\mathbf{L}^{phen3}$), which is probably due to a decrease in the electron density of the heteroaromatic ring caused by introducing the cationic metal fragments (Fig. 3). Similar to the ligand NMR data, only one set of signals for the ethyl, methylene or ethylene moieties and the tethered metal fragments were observed, which agrees with the pseudo-C_3 symmetry of the trinuclear complexes. In the spectra of the dinuclear complexes, characteristic NMR signals for the protons (δ_H (H17 for **8–10**, H22 for **11–12**) ~7.0 (singlet)) and the carbon atoms of the phenyl ring (δ_C (C17 for **8–10**, C22 for **11,12**) ~130 (doublet)) were observed. Compared to ethylene-bridged complexes **4–7**, the methylene-bridged complexes showed broad signals, probably due to dynamic behavior (*vide infra*).

The IR spectra of the Rh carbonyl complexes in nitromethane solution exhibited two C–O stretching bands at 2100 and 2038 cm^{-1} for the pypz complexes **3** and **10**, and 2096 and 2034 cm^{-1} for the phenanthroline complex **7**. These wavenumbers are similar to those of the corresponding mononuclear model complexes $[(pypz^{Me})Rh(CO)_2]BF_4$ ($pypz^{Me}$ = 1-Me-3-(2-pyridyl)pyrazole, ν_{CO} = 2100, 2038 cm^{-1}) and $[(bpy)Rh(CO)_2]BF_4$ (ν_{CO} = 2100, 2040 cm^{-1}), suggesting that the metal centers have a similar electron density, irrespective of the numbers of metal fragments incorporated.

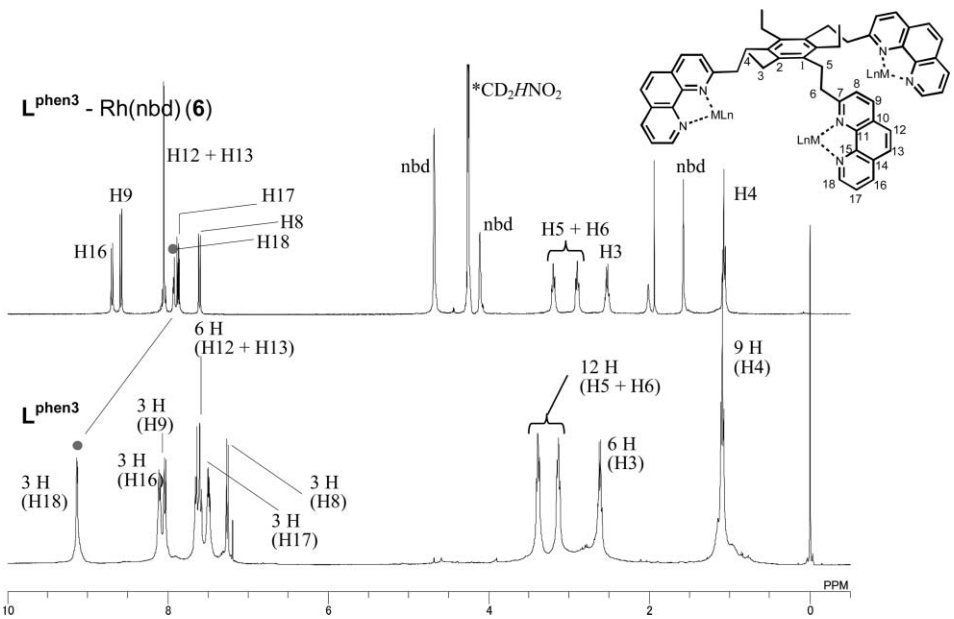

Fig. 3 ^{1}H NMR spectra of **6** and $\mathbf{L}^{phen3}$.

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Although we were unable to obtain single crystals of the ethylene-bridged compounds, crystals of the methylene-bridged ligand $\mathbf{L}^{pypz3}$, **1**, and **2** were obtained, and their structures were determined by using single crystal X-ray crystallography.† The crystal data and data collection parameters are given in Table 1, and top and side views of $\mathbf{L}^{pypz3}$ and the cations of **1** and **2** are shown in Fig. 4. Although $\mathbf{L}^{pypz3}$ has an *ababba* configuration, complexes **1** and **2** have an *ababab* configuration, which is generally seen for the structures of 2,4,6-trisubstituted 1,3,5-triethylbenzene compounds.[7a,c,e,f,8b,e,10] In the solid state structures of **1** and **2**, the pypz–metal side arms are below the benzene plane, and the Pd–allyl and Rh–cod fragments point toward the outside of the complex to relieve steric repulsion. Preliminary crystal structure determination of the dinuclear Pd–allyl complex **8** showed that both of the pypz metal side arms are also below the benzene core and the conformation adopted by the ligand is very similar to that of **1**, although one of the ethyl substituents adjacent to the phenyl H was directed downward. The Pd–N bond lengths and N–Pd–N bond angles are similar to those of the corresponding mononuclear complexes, such as $[(pypz)PdCl_2]$[11] and $[(pypz^{Me})Rh(cod)PPh_3]OTf$.[12] The angles at the methylene group connecting the pypz ligand and the benzene core (∠C(phenyl)–C(methylene)–N(pyrazole)) are summarized in Table 2. The averaged bond angles were 111.2°, 110.6°, and 111.1° for $\mathbf{L}^{pypz3}$, **1**, and **2**, respectively, and the differences in the angles between the ligands and di- and trinuclear complexes was less than 1°. This result shows that the steric hindrance caused by introduction of the metal fragments is avoided by rotation of the metal fragment around the CH_2–N bond.

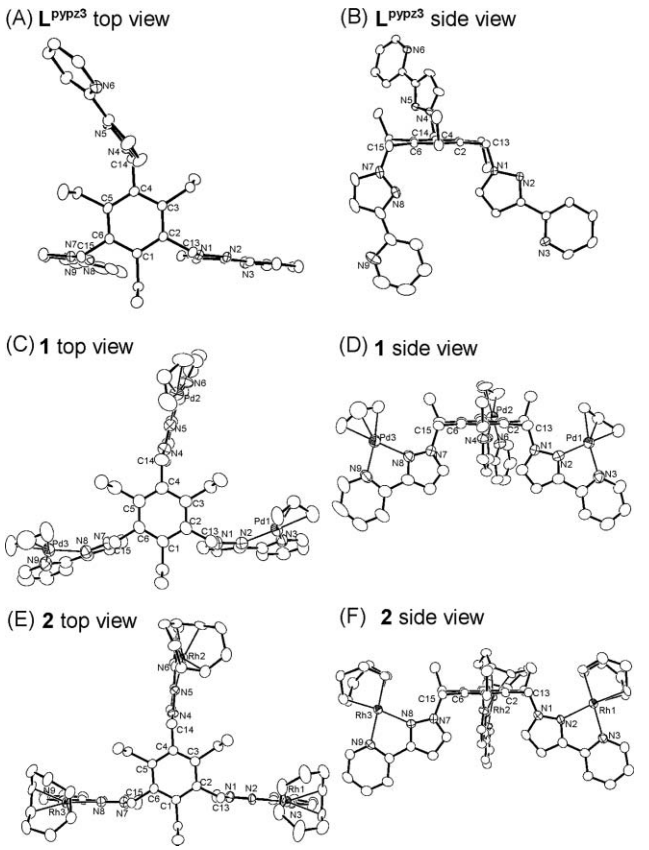

Fig. 4 ORTEP representation (top and side views) of $\mathbf{L}^{pypz3}$, **1**, and **2** with thermal ellipsoids at 30% probability. H atoms are omitted for clarity.

Fluxional behavior

No ^{1}H NMR spectral changes were observed for the ethylene-bridged trinuclear complexes (**4**–**7**) in the temperature range of −40 to 65 °C, suggesting fast rotation of the ethyl and ethylene–ML groups around the C(phenyl)–CH_2 bonds. In contrast, the methylene-bridged complexes displayed broad signals at room temperature, which led us to further investigate their fluxional behavior. VT ^{1}H NMR spectra (500 MHz) of the trinuclear Rh–carbonyl complex **3** were recorded in CD_3NO_2 in the temperature

Table 1 Crystallographic data for $\mathbf{L}^{pypz3}$, **1**, and **2**

	$\mathbf{L}^{pypz3}$	$\mathbf{L}^{pypz3}$-Pd(allyl) (**1**)	$\mathbf{L}^{pypz3}$-Rh(cod) (**2**)
Formula	$C_{39}H_{39}N_9$	$C_{51}H_{63}B_3F_{12}N_{12}O_6Pd_3$	$C_{65}H_{81}B_3F_{12}N_{11}O_4Rh_3$ +0.5(CH_3NO_2)
Formula weight	633.80	1519.76	1680.09
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P21/n$ (#14)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)
a/Å	11.3126(6)	13.074(8)	14.304(3)
b/Å	26.386(2)	15.005(9)	14.663(5)
c/Å	12.211(1)	17.337(9)	18.456(6)
α/°	90	105.76(4)	104.890(11)
β/°	109.579(4)	97.23(4)	90.88(2)
γ/°	90	110.73(2)	108.688(16)
V/Å^3	3434.1(5)	2967(3)	3523.5(19)
Z	4	2	2
d_{calc}/g cm^{-3}	1.226	1.701	1.584
Temp./°C	−60	−60	−60
Radiation	MoKα ($\lambda = 0.71069$ Å)	MoKα ($\lambda = 0.71069$ Å)	MoKα ($\lambda = 0.71069$ Å)
μ/cm^{-1}	7.60	9.96	7.83
Diffractometer	Rigaku RAXIS IV	Rigaku RAXIS IV	Rigaku RAXIS IV
Max 2θ/°	55.0	55.0	55.0
Reflections collected; independent reflections	27257; 7173 [R(int) = 0.061]	15780; 10416 [R(int) = 0.0757]	25478; 14223 [R(int) = 0.0880]
No. of parameters refined	591	694	895
$R1$ ($I > 2\sigma$) (%)	4.57	7.52	8.92
wR_2 (all) (%)	12.2	22.64	27.26
Goodness of fit	1.031	0.904	1.060

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Table 2 Selected bond angles (°)

	∠N1–C13–C2	∠N4–C14–C4	∠N7–C15–C6	Average
$\mathbf{L}^{pypz3}$	112.31(10)	110.4(1)	110.9(1)	111.2
1	109.7(7)	111.9(7)	110.2(6)	110.6
2	111.3(5)	110.6(6)	111.3(5)	111.1

range of −25 to 65 °C (Fig. 5). The ^{1}H NMR spectrum measured at room temperature contained broad signals for the methyl and methylene protons of the ethyl groups and pyrazolyl protons (H6), whereas those of the other protons were relatively sharp. As the temperature was raised, the broad signals changed into a single set of sharp signals, indicating C_3 symmetry on the NMR timescale. The broad singlet for the methyl groups at ambient temperature decoalesced at 0 °C, and the spectrum at −25 °C displayed two inequivalent singlets ($\delta\nu$ = 218 Hz) with an integral ratio of 3 : 1. Using the data, the barrier for the rotation process on the C–C axis was calculated to be 12.6 kcal mol^{-1} at the coalescence temperature.[13] The methylene (of the ethyl group) and the pyrazolyl-H (H6) signals also split into two inequivalent signals at this temperature, whereas the other signals did not show any significant changes in the temperature range. The inequivalent signals suggest the presence of at least two conformational isomers, such as those shown in Fig. 6. Interconversion among the isomers was frozen below −25 °C, and thus, signals for protons in different magnetic environments

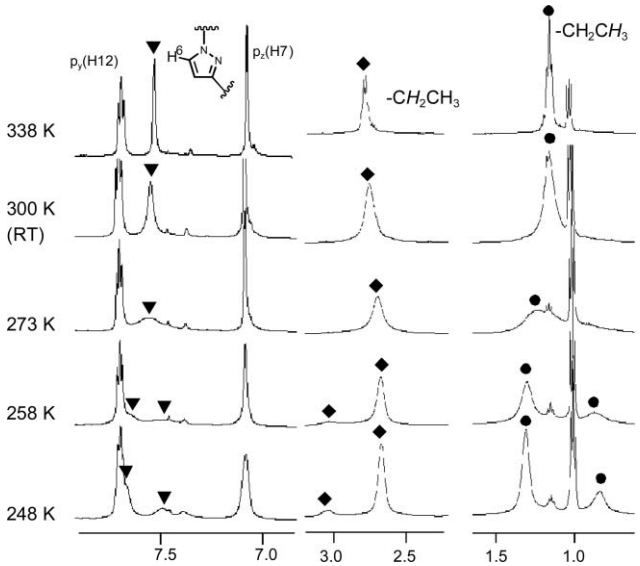
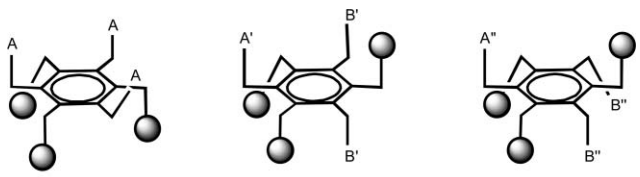


Fig. 5 500 MHz VT ^{1}H NMR spectra of the ethyl and aromatic region of **3** at 338, 300, 273, 258 and 248 K.



(I) *ababab* II(i) *abbaab* II(ii) *abbabb*

Fig. 6 Possible conformational isomers observed at low temperature.

(such as H^A, $H^{A'}$, $H^{A''}$ and $H^{B'}$, $H^{B''}$) were observed at different chemical shifts. Unfortunately, further investigation was hampered by the high melting point of the deuterated nitromethane.[14] The VT NMR study shows the dynamic behavior of the metal fragment $[(pypz)Rh(CO)_2]^+$ around the C(phenyl)–CH_2 bond, similar to those reported for the tetra- and triethyl substituted benzene compounds, such as 1,4-dineohexyl-2,3,5,6-tetraethylbenzene and its chromium tricarbonyl complex.[15] The rotational barrier around the C–C axis is slightly larger than the corresponding barriers for the various 1,4-disubstituted η^6-2,3,5,6-tetraethylbenzene Cr carbonyl complexes.[15]

The lack of changes in the VT NMR spectra observed for the ethylene-bridged complexes indicates much lower energy barriers for the C–C bond rotation, because of the reduced steric congestion among the tether parts, due to the longer linkers. In addition, the VT NMR study shows that the bulky metal centers of the methylene- and ethylene-bridged tethers can interact with substrates due to C(phenyl)–CH_2 bond rotation.

Summary

New di- and trinucleating ligands having N,N-chelating tethers with different chain lengths incorporated at the 2, 4 and 6 positions of the 1,3,5-triethylbenzene backbone, which readily reacted with various Pd and Rh precursors to form di- and trinuclear complexes, were synthesized. X-Ray structural studies showed that the trinuclear complexes with methylene-bridged pypz ligands adopt an *ababab* configuration, in which the metal fragments are beneath the benzene plane. VT ^{1}H NMR studies showed that the methylene-bridged tethers rotate around the C(phenyl)–CH_2 bonds, causing inequivalent sets of ethyl and pyrazolyl proton signals at low temperature. These results indicate that the structures are flexible, which may allow multiple metal centers to interact with substrates in a concerted manner under ambient reaction conditions. From a comparison of the complexes having ethylene-bridged ligands ($\mathbf{L}^{phen3}$, $\mathbf{L}^{phen3'}$, and $\mathbf{L}^{phen2}$) with those of methylene-bridged ones, the rotational barrier of the C(phenyl)–CH_2 bond seems to be much smaller for the ethylene-bridged complexes, because of the reduced steric repulsion between the metal fragments and the ethyl substituents due to the longer carbon chains.

Experimental

General

Standard Schlenk and vacuum line techniques under N_2 atmosphere were employed for the reactions. Acetone (molecular sieves), acetonitrile (P_2O_5), and nitromethane ($CaCl_2$) were treated with appropriate drying agents, distilled, and stored under N_2. The metal reagents $[Pd(C_3H_5)cod]BF_4$,[16] $[Rh(cod)_2]BF_4$,[17] and $[Rh(nbd)_2]BF_4$[17] were prepared according to the published procedures. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC-200, JEOL GX-270, JEOL EX-400, and JEOL LA-500 spectrometers. Solvents for NMR measurements were dried over molecular sieves, degassed, and stored under N_2. IR spectra were obtained on a JASCO FT/IR 5300 spectrometer. ESI-MS and HRMS (FAB) spectra were recorded on a ThermoQuest Finnigan LCQ Duo mass spectrometer and a JEOL JMS-700 mass spectrometer,

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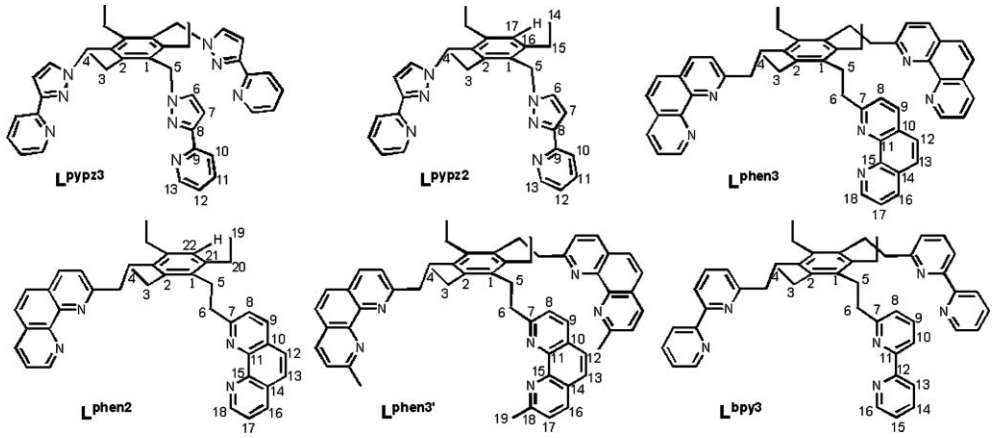

Chart 1 NMR labeling scheme of the ligands and the corresponding tri- and dinuclear complexes.

respectively. Other chemicals were purchased and used as received. In the following section, $^3J_{HH}$ and $^1J_{CH}$ are abbreviated as J and J_{CH}, respectively. The NMR labeling scheme of the ligands and the corresponding tri- and dinuclear complexes is given in Chart 1.

Preparation of L^{pypz3}. Tri(chloromethyl)triethylbenzene (662 mg, 2.15 mmol) and 3-(2-pyridyl)pyrazole (1.03 g, 7.10 mmol) were dissolved in toluene (50 mL), and 40% NaOH aq (7 mL) and 40% NBu_4OH solution (a few drops) were added to the solution. The mixture was heated at 90 °C for 7 h. The organic layer was extracted with toluene and dried over $MgSO_4$, filtered, and rotary evaporated to dryness to yield the crude product. The product was recrystallized from Et_2O–pentane (white crystals, 1.25 g, 1.98 mmol, 92% yield). ^{1}H NMR (400 MHz, acetone-d_6): δ 8.40 (d, $J = 4.1$ Hz, 3 H, H13), 7.83 (d, $J = 8.1$ Hz, 3 H, H10), 7.61 (t, $J = 7.7$ Hz, 3 H, H11), 7.27 (d, $J = 2.2$ Hz, 3 H, H6), 7.08 (d, $J = 7.6$ Hz, 3 H, H12), 6.70 (d, $J = 2.4$ Hz, 3 H, H7), 5.46 (s, 6 H, H5), 2.83 (q, $J = 7.6$ Hz, 6 H, H3), 0.92 (t, $J = 7.6$ Hz, 9 H, H4). ^{13}C NMR (100 MHz, acetone-d_6): δ 153.5 (s, C9), 152.6 (s, C1), 150.1 (d, $J_{CH} = 176$ Hz, C13), 147.0 (s, C8), 137.1 (d, $J_{CH} = 160$ Hz, C11), 131.5 (s, C2), 131.0 (d, $J_{CH} = 180$ Hz, C6), 123.0 (d, $J_{CH} = 162$ Hz, C12), 120.1 (d, $J_{CH} = 165$ Hz, C10), 104.9 (d, $J_{CH} = 177$ Hz, C7), 50.6 (t, $J_{CH} = 140$ Hz, C5), 24.0 (t, $J_{CH} = 126$ Hz, C3), 15.7 (q, $J_{CH} = 121$ Hz, C4). HRMS (FAB, pos): $m/z = 634.3421$ (calcd for $[M + H]^+$, $C_{39}H_{40}N_9$ 634.3407).

Preparation of L^{pypz2}. Di(bromomethyl)triethylbenzene (1.0 g, 2.87 mmol) and 3-(2-pyridyl)pyrazole (834 mg, 5.74 mmol) were dissolved in toluene (50 mL), and 40% NaOH aq (7 mL) and 40% NBu_4OH solution (a few drops) were added to the solution. The mixture was heated at 90 °C for 7 h. The organic layer was extracted with toluene and dried over $MgSO_4$, filtered, and rotary evaporated to dryness to yield the crude product. The product was recrystallized from CH_2Cl_2–hexane (white crystals, 848 mg, 1.78 mmol, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (d, $J = 3.6$ Hz, 2 H, H17), 7.81 (d, $J = 7.8$ Hz, 2 H, H14), 7.54 (t, $J = 7.1$ Hz, 2 H, H15), 7.03–7.00 (m, 3 H, H1 + H16), 6.89 (d, $J = 2.2$ Hz, 2 H, H10), 6.70 (d, $J = 2.2$ Hz, 2 H, H11), 5.38 (s, 4 H, H9), 2.64 (q, $J = 7.6$ Hz, 2 H, H7), 2.56 (q, $J = 7.6$ Hz, 4 H, H5), 1.05 (t, $J = 7.6$ Hz, 6 H, H6), 0.90 (t, $J = 7.6$ Hz, 3 H, H8). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.5 (s, C13), 150.9 (s, C3), 148.5 (d, $J_{CH} = 178$ Hz, C17), 144.6 (s, C4), 143.9 (s, C12), 135.6 (d, $J_{CH} = 161$ Hz, C15), 128.7 (d, $J_{CH} = 172$ Hz, C10), 127.7 (s, C2), 127.2 (d, $J_{CH} = 156$ Hz, C1), 121.4 (d, $J_{CH} = 163$ Hz, C16), 119.1 (d, $J_{CH} = 163$ Hz, C14), 103.4 (d, $J_{CH} = 178$ Hz, C11), 48.8 (t, $J_{CH} = 140$ Hz, C5), 25.4 (t, $J_{CH} = 126$ Hz, C5), 22.1 (t, $J_{CH} = 126$ Hz, C7), 14.8 (q, $J_{CH} = 128$ Hz, C8), 14.5 (q, $J_{CH} = 127$ Hz, C6). HRMS (FAB, pos): $m/z = 477.2763$ (calcd for $[M + H]^+$, $C_{39}H_{40}N_9$ 477.2767).

Preparation of L^{phen3}. A THF solution of 2-methyl-1,10-phenanthroline (440 mg, 2.59 mmol) was added to 1.2 equiv of LDA–THF solution at −78 °C and stirred for 2 h at this temperature. After addition of a tri(chloromethyl)triethylbenzene (256 mg, 0.84 mmol)–THF solution, the solution was stirred at −8 °C for 4 h and then at ambient temperature for 12 h. The volatiles were removed under reduced pressure after the solution was quenched with H_2O (20 mL) and the reddish brown precipitate was extracted with CH_2Cl_2 (50 mL × 3), washed with saturated NaCl aq, dried with Na_2SO_4, and evaporated. The residual oil was purified by column chromatography (silica, $CH_2Cl_2 \rightarrow CH_2Cl_2$: MeOH = 9 : 1) and recrystallization with CH_2Cl_2–hexane to yield L^{phen3} as a reddish brown solid (260 mg, 0.33 mmol, 40%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.20 (d, $J = 4.1$ Hz, 3 H, H18), 8.17 (d, $J = 8.1$ Hz, 3 H, H16), 8.10 (d, $J = 8.3$ Hz, 3 H, H9), 7.72–7.67 (m, 6 H, H12 + H13), 7.57–7.54 (m, 3 H, H17), 7.32 (d, $J = 8.3$ Hz, 3 H, H8), 3.45 (t, $J = 8.3$ Hz, 6 H, H5 or H6), 3.20 (t, $J = 7.8$ Hz, H5 or H6), 2.68 (q, $J = 7.2$ Hz, 6 H, H3), 1.16 (t, $J = 7.2$ Hz, 9H, H4). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.5 (s, C7), 150.0 (d, $J_{CH} = 179$ Hz, C18), 146.0 (s, C15), 145.6 (s, C11), 139.4 (s, C1), 136.0 (d, $J_{CH} = 161$ Hz, C9), 135.9 (d, $J_{CH} = 161$ Hz, C16), 135.1 (s, C2), 128.7 (s, C14), 127.0 (s, C10), 126.4 (d, $J_{CH} = 162$ Hz, C13), 125.5 (d, $J_{CH} = 162$ Hz, C12), 122.7 (d, $J_{CH} = 161$ Hz, C8), 122.5 (d, $J_{CH} = 164$ Hz, C17), 40.8 (t, $J_{CH} = 128$ Hz, C5 or C6), 29.1 (t, $J_{CH} = 128$ Hz, C5 or C6), 22.6 (t, $J_{CH} = 125$ Hz, C3), 15.8 (q, $J_{CH} = 127$ Hz, C4). HRMS: calcd for $[M + H]^+$: 781.4109, found 781.4042.

Preparation of L^{phen2}. The ligand was synthesized in a similar manner as L^{phen3} by treating 2-methyl-1,10-phenanthroline and 1.2 equiv of LDA with di(bromomethyl)triethylbenzene at a ratio of 2 : 1 (268 mg, 0.47 mmol, 14%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.20 (d, $J = 4.1$ Hz, 2 H, H18), 8.20 (d, $J = 8.0$ Hz, 2 H, H16), 8.08 (d, $J = 8.3$ Hz, 2 H, H9), 7.74–7.67 (m, 4 H, H12 + H13), 7.59–7.56 (m, 2 H, H17), 7.35 (d, $J = 8.3$ Hz, 2 H, H9), 6.91 (s, 1 H, H22), 3.37 (t, $J = 7.6$ Hz, 4 H, H5 or H6), 3.15 (t, $J = 7.6$ Hz, 4 H, H5 or H6), 2.69–2.60 (m, 6 H, H20 + H3), 1.20 (t, $J = 7.6$ Hz,

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6 H, H19), 1.09 (t, J = 7.6 Hz, 3 H, H4). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.4 (s, C7), 149.9 (d, J_{CH} = 179 Hz, C18), 145.7 (s, C15), 145.4 (s, C10), 140.6 (s, C2), 140.2 (s, C21), 135.9 (d, J_{CH} = 161 Hz, C9), 135.7 (d, J_{CH} = 161 Hz, C16), 134.4 (s, C1), 128.5 (s, C14), 126.8 (s, C11), 126.3 (d, J_{CH} = 157 Hz, C22), 126.2 (d, J_{CH} = 162 Hz, C13), 125.3 (d, J_{CH} = 162 Hz, C12), 122.5 (d, J_{CH} = 161 Hz, C8), 122.4 (d, J_{CH} = 163 Hz, C17), 40.3 (t, J_{CH} = 128 Hz, C5 or C6), 28.9 (t, J_{CH} = 127 Hz, C5 or C6), 25.6 (t, J_{CH} = 126 Hz, C20), 22.3 (t, J_{CH} = 125 Hz, C3), 15.8 (q, J_{CH} = 126 Hz, C4), 15.3 (q, J_{CH} = 127 Hz, C19). HRMS: calcd for $[M + H]^+$: 575.3175, found: 575.3175.

Preparation of $L^{phen3\prime}$. The ligand was synthesized in a similar manner as L^{phen3} by using 2,9-dimethyl-1,10-phenanthroline (1.00 g, 4.80 mmol) with 1.2 equiv of LDA and tri(chloromethyl)-triethylbenzene (492 mg, 1.60 mmol) to yield $L^{phen3\prime}$ (329 mg, 0.40 mmol, 25%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08–7.96 (m, 6 H, H9 + H16), 7.62–7.54 (m, 6 H, H12 + H13), 7.42–7.34 (m, 6 H, H8 + H17), 3.40 (t, J = 8.1 Hz, 6 H, H5 or H6), 3.22 (t, J = 8.0 Hz, 6 H, H5 or H6), 2.85 (brs, 9 H, H19), 2.83 (brs, 6 H, H3), 1.22 (t, J = 7.2 Hz, 9 H, H4). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.6 (s, C7), 158.3 (s, C18), 144.6 (s, C15), 144.4 (s, C11), 138.9 (s, C1), 135.8 (d, J_{CH} = 161 Hz, C9), 135.5 (d, J_{CH} = 161 Hz, C16), 135.0 (s, C2), 126.5 (s, C14), 126.0 (s, C10), 124.8 (d, J_{CH} = 162 Hz, C13), 124.6 (d, J_{CH} = 162 Hz, C12), 122.7 (d, J_{CH} = 161 Hz, C8), 121.8 (d, J_{CH} = 164 Hz, C17), 40.3 (t, J_{CH} = 128 Hz, C5 or C6), 29.1 (t, J_{CH} = 128 Hz, C5 or C6), 25.0 (q, J_{CH} = 126 Hz, C19), 22.2 (t, J_{CH} = 125 Hz, C3), 15.5 (q, J_{CH} = 127 Hz, C4).

Preparation of L^{bpy3}. 6-Methyl-2,2′-bipyridine was synthesized according to the published method.[18] The ligand L^{bpy3} was synthesized in a similar manner as L^{phen3} by treating 1.62 g (9.52 mmol) of 6-methyl-2,2′-bipyridine and 1.2 equiv of LDA with tri(chloromethyl)triethylbenzene 500 mg (1.63 mmol) to yield the ligand as a reddish brown solid (400 mg, 0.52 mmol, 32%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (d, J = 4.3 Hz, 3 H, H16), 8.42 (d, J = 7.8 Hz, 3 H, H13), 8.15 (d, J = 7.8 Hz, 3 H, H10), 7.54 (t, J = 7.8 Hz, 3 H, H14), 7.52 (t, J = 7.8 Hz, 3 H, H9), 7.03–7.01 (m, 6 H, H8 + H15), 3.06, 3.00 (s, 12 H, H5 + H6), 2.85 (q, J = 7.0 Hz, 6 H, H3), 1.20 (t, J = 7.0 Hz, 9 H, H4). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.1 (s, C7), 156.5 (s, C11), 155.5 (s, C12), 149.0 (d, J_{CH} = 177 Hz, C16), 139.1 (s, C1), 137.2 (d, J_{CH} = 161 Hz, C9), 136.8 (d, J_{CH} = 161 Hz, C14), 135.6 (s, C2), 123.5 (d, J_{CH} = 163 Hz, C15), 122.4 (d, J_{CH} = 161 Hz, C8), 121.0 (d, J_{CH} = 165 Hz, C10), 118.3 (d, J_{CH} = 165 Hz, C13), 40.1 (t, J_{CH} = 128 Hz, C5 or C6), 29.8 (t, J_{CH} = 128 Hz, C5 or C6), 22.6 (t, J_{CH} = 125 Hz, C3), 15.9 (q, J_{CH} = 127 Hz, C4).

Synthesis of 1. L^{pypz3} (46 mg, 73 μmol) and $[Pd(C_3H_5)cod]BF_4$ (78 mg, 230 μmol) were dissolved in CH_3NO_2 (5 mL) and stirred at ambient temperature for 1 h. The volatiles were evaporated and the residual solid was washed with Et_2O and hexane to remove the free cod ligand. The solid was dried under vacuum to yield the white solid, which was used without further purification (66 mg, 51 μmol, 70% yield). ^{1}H NMR (200 MHz, CD_3NO_2): δ 8.75 (d, J = 4.9 Hz, 3 H, H13), 8.17 (t, J = 7.8 Hz, 3 H, H11), 8.07 (d, J = 7.9 Hz, 3 H, H10), 7.58 (t, J = 6.5 Hz, 3 H, H12), 7.46 (d, J = 2.7 Hz, 3 H, H6), 7.06 (d, J = 2.7 Hz, 3 H, H7), 6.02 (m, 3 H, C_3H_5), 5.68 (m, 6 H, H5), 4.81, 4.54 (d, J = 5.9 Hz, 6 H, C_3H_5-*syn*), 3.78, 3.51 (d, J = 12.4, 12.2 Hz, 6 H, C_3H_5-*anti*), 2.78–2.70 (brs, 6 H, H3), 1.15–1.22 (brs, 9 H, H4). ^{13}C NMR (100 MHz, CD_3NO_2): δ 155.1 (d, J_{CH} = 185 Hz, C13), 154.1 (s, C9), 151.8 (s, C1), 149.3 (s, C8), 142.3 (d, J_{CH} = 168 Hz, C11), 134.9 (d, J_{CH} = 193 Hz, C6), 130.7 (s, C2), 127.5 (d, J_{CH} = 170 Hz, C12), 123.5 (d, J_{CH} = 169 Hz, C10), 119.8 (d, J_{CH} = 165 Hz, C_3H_5), 106.4 (d, J_{CH} = 184 Hz, C7), 59.9, 67.0 (t, J_{CH} = 155, 164 Hz, C_3H_5), 53.3 (t, J_{CH} = 144 Hz, C5), 24.7 (t, J_{CH} = 128 Hz, C3), 15.6 (q, J_{CH} = 128 Hz, C4). ESI-MS (MeCN): m/z = 781.2 $[(L^{pypz3})Pd(C_3H_5)]^+$, 1249.9 $[(L^{pypz3})Pd_3(C_3H_5)_3(BF_4)_2]^+$. Anal. calcd for $C_{48}H_{54}B_3F_{12}N_9Pd_3$: C, 43.13; H, 4.07; N, 9.43. Found: C, 42.90; H, 4.51; N, 9.61%.

Synthesis of 2. A mixture of $[Rh(cod)_2]BF_4$ (198 mg, 0.487 mmol) and L^{pypz3} (100 mg, 0.157 mmol) in CH_3NO_2 (5 mL) was stirred at ambient temperature for 2 h. After the solvent was removed under vacuum, the product was washed with Et_2O (20 mL × 3), dried under vacuum to give **2** as orange crystalline solid. ^{1}H NMR (200 MHz, CD_3NO_2): δ 8.11 (t, J = 7.6 Hz, 3 H, H11), 7.97 (d, J = 7.4 Hz, 3 H, H10), 7.80 (d, J = 5.5 Hz, 3 H, H13), 7.55 (t, J = 6.1 Hz, 3 H, H12), 7.26 (s, 3 H, H6), 6.93 (d, J = 2.7 Hz, 3 H, H7), 5.30 (s, 6 H, H5), 4.94 (s, 12 H, -C*H*=C*H*- (cod)), 2.10–2.62 (m, 30 H, H3 + -CH_2- (cod)), 1.29 (t, J = 7.4 Hz, 9 H, H4). ^{13}C NMR (100 MHz, CD_3NO_2): δ 156.4 (s, C9), 153.0 (s, C1), 149.5 (s, C8), 149.0 (d, J_{CH} = 184 Hz, C13), 142.6 (d, J_{CH} = 171 Hz, C11), 136.4 (d, J_{CH} = 187 Hz, C6), 130.5 (s, C2), 127.3 (d, J_{CH} = 174 Hz, C12), 123.6 (d, J_{CH} = 172 Hz, C10), 106.3 (d, J_{CH} = 187 Hz, C7), 84.8 (d, J_{CH} = 150 Hz, -*C*H=*C*H= (cod)), 50.6 (t, J_{CH} = 144 Hz, C5), 31.6 (t, J_{CH} = 130 Hz, -*C*H_2- (cod)), 24.6 (t, J_{CH} = 128 Hz, C3), 15.7 (q, J_{CH} = 128 Hz, C4). ESI-MS (MeCN): m/z = 844.8 $[(L1)Rh(cod)]^+$, 1440.7 $[(L^{pypz3})Rh_3(cod)_3(BF_4)_2]^+$. Elemental analysis data could not be obtained due to the instability of the complex.

Synthesis of 3. A CH_3NO_2 solution (5 mL) of **2** (200 mg, 0.131 mmol) was degassed by a freeze–pump–thaw procedure. After an atmospheric pressure of CO gas was introduced, the reaction mixture was cooled by ice bath and was stirred for 1 h. The resulting yellow solution was precipitated by addition of Et_2O. Then the precipitate was dissolved in CH_3NO_2, filtered through celite and reprecipitated, and then dried under vacuum to yield **3** as a reddish brown solid (144 mg, 0.104 mmol, 80% yield). ^{1}H NMR (200 MHz, CD_3NO_2): δ 8.78 (d, J = 5.6 Hz, 3 H, H13), 8.28 (d, J = 7.8 Hz, 3 H, H11), 8.09 (d, J = 7.6 Hz, 3 H, H10), 7.68 (t, J = 5.7 Hz, 3 H, H12), 7.49 (d, J = 2.3 Hz, 3 H, H6), 7.05 (d, J = 2.7 Hz, 3 H, H7), 5.81 (s, 6 H, H5), 2.78 (brs, 6 H, H3), 1.19 (brs, 9 H, H4). ^{13}C NMR (100 MHz, CD_3NO_2): δ 184.5 (d, $J_{Rh\text{-}C}$ = 70 Hz, *C*O), 154.0 (d, J_{CH} = 184 Hz, C13), 155.3 (C9), 150.9 (s, C1), 148.8 (s, C8), 142.8 (d, J_{CH} = 171 Hz, C11), 135.7 (d, J_{CH} = 198 Hz, C6), 128.6 (s, C2), 126.9 (d, J_{CH} = 172 Hz, C12), 122.8 (d, J_{CH} = 172 Hz, C10), 105.6 (d, J_{CH} = 187 Hz, C7), 51.9 (t, J_{CH} = 144 Hz, C5), 23.4 (t, J_{CH} = 128 Hz, C3), 14.1 (q, J_{CH} = 128 Hz, C4). IR (CH_3NO_2 solution) ν_{CO} = 2100, 2038 cm^{-1}. ESI-MS (MeCN): m/z = 792.7 $[(L^{pypz3})Rh(CO)_2]^+$, 1284.2 $\{[(L1)(Rh(CO)_2)_3](BF_4)_2\}^+$. Anal. calcd for $C_{45}H_{39}B_3F_{12}N_9O_6Rh_3$ + Me_2CO: C, 40.34; H, 3.17; N, 8.82. Found: C, 40.39; H, 3.43; N, 8.95%.

Synthesis of 4. To a CH_2Cl_2 solution of $[Pd(C_3H_5)cod]BF_4$ (263 mg, 0.768 mmol), L^{phen3} (100 mg, 0.256 mmol) was added and the mixture immediately became cloudy. The solution was stirred for 1 h and the white precipitate was collected by filtration. The filtrate was washed with Et_2O and hexane. Drying under vacuum

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yielded **4** as a white solid (171 mg, 0.115 mmol, 45%). ^{1}H NMR (400 MHz, CD_3NO_2): δ 9.30 (d, J = 5.2 Hz, 3 H, H18), 8.93 (d, J = 8.3 Hz, 3 H, H16), 8.81 (d, J = 8.5 Hz, 3 H, H9), 8.25–8.20 (m, 6 H, H12 + H13), 8.13–8.10 (m, 3 H, H17), 7.98 (d, J = 8.5 Hz, 3 H, H8), 6.02 (m, J = 6.6 Hz, 3 H, C_3H_5), 4.63, 4.54 (d, J = 6.8, 7.1 Hz, 6 H, C_3H_5-*syn*), 3.81 (t, J = 7.8 Hz, 6 H, H5 or H6), 3.97, 3.58 (d, J = 13.2, 12.0 Hz, 6 H, C_3H_5), 3.46 (t, J = 7.9 Hz, 6 H, H5 or H6), 2.74 (q, J = 7.2 Hz, 6 H, H3), 1.23 (t, J = 7.2 Hz, 9 H, H4). ^{13}C NMR (100 MHz, CD_3NO_2): δ 165.8 (s, C7), 155.0 (d, J_{CH} = 187 Hz, C18), 147.0 (s, C15), 146.5 (s, C11), 141.6 (d, J_{CH} = 167 Hz, C9), 141.0 (d, J_{CH} = 167 Hz, C16), 140.9 (s, C1), 135.5 (s, C2), 131.7 (s, C14), 130.0 (s, C10), 128.9 (d, J_{CH} = 167 Hz, C13), 127.9 (d, J_{CH} = 167 Hz, C12), 127.0 (d, J_{CH} = 171 Hz, C8), 127.0 (d, J_{CH} = 170 Hz, C17), 119.8 (t, J_{CH} = 163 Hz, C_3H_5), 67.6 (t, J_{CH} = 162 Hz, C_3H_5), 46.0 (t, J_{CH} = 128 Hz, C5 or C6), 30.0 (t, J_{CH} = 130 Hz, C5 or C6), 24.3 (t, J_{CH} = 128 Hz, C3), 16.2 (q, J_{CH} = 129 Hz, C4). ESI-MS(MeCN) m/z = 1162.8 [$(\mathbf{L}^{phen3})Pd_2(C_3H_5)_2(BF_4)$]$^+$, 1397.1 [$(\mathbf{L}^{phen3})Pd_3(C_3H_5)_3(BF_4)_2$]$^+$. Anal. calcd for $C_{63}H_{63}N_6Pd_3 + (BF_4)_3$. C; 50.99, H; 4.28, N; 5.66. Found: C; 50.54, H; 4.44, N; 5.54%.

Synthesis of 5. To a CH_2Cl_2 (2 mL) + MeCN (3 mL) solution of (cod)PdMeCl (104 mg, 0.39 mmol), $\mathbf{L}^{phen3}$ (100 mg, 0.128 mmol) was added dropwise. After the solution was stirred at room temperature, AgOTf (115 mg, 0.445 mmol) was added and the mixture was stirred for another 1 h. The reaction mixture was filtered through Celite and the volatiles of the filtrate were removed under reduced pressure. The crude product was washed with Et_2O and CH_2Cl_2 to yield **5** as a yellowish brown solid (147 mg, 0.086 mmol, 67%). ^{1}H NMR (400 MHz, CD_3NO_2): δ 8.80 (d, J = 5.2 Hz, 3 H, H18), 8.61 (d, J = 7.6 Hz, 3 H, H16), 8.52 (d, J = 8.0 Hz, 3 H, H9), 7.91–8.00 (m, 6 H, H12 + H13), 7.83 (brs, 3 H, H17), 7.57 (d, J = 7.8 Hz, 3 H, H8), 3.39 (brs, 6 H, H5 or H6), 3.22 (brs, 6 H, H5 or H6), 2.65 (brs, 6 H, H3), 2.25 (brs, 9 H, *Me*CN), 1.26 (brs, 9 H, Pd-*Me*), 1.04 (t, J = 7.1 Hz, 9 H, H4). ^{13}C NMR (100 MHz, CD_3NO_2): δ 165.7 (s, C7), 150.3 (d, J_{CH} = 168 Hz, C18), 148.3 (s, C15), 144.9 (s, C11), 142.0 (d, J_{CH} = 165 Hz, C9), 141.5 (d, J_{CH} = 164 Hz, C16), 140.4 (s, C1), 136.4 (s, C2), 132.1 (s, C14), 129.8 (s, C10), 129.2 (d, J_{CH} = 167 Hz, C13), 127.9 (d, J_{CH} = 168 Hz, C12), 127.6 (d, J_{CH} = 174 Hz, C8), 126.4 (d, J_{CH} = 163 Hz, C17), 41.5 (t, J_{CH} = 128 Hz, C5 or C6), 29.9 (t, J_{CH} = 130 Hz, C5 or C6), 24.0 (t, J_{CH} = 128 Hz, C3), 16.6 (q, J_{CH} = 121 Hz, C4), 7.5 (q, J_{CH} = 139 Hz, *Me*CN), 3.7 (q, J_{CH} = 136 Hz, Pd-*Me*). ESI-MS (MeCN): m/z = 1413.4 [$(\mathbf{L}^{phen3})Pd_3Me(OTf)_2$]$^+$, 1428.5 [$(\mathbf{L}^{phen3})Pd_3Me_2(OTf)_2$]$^+$, 1443.5 [$(\mathbf{L}^{phen3})Pd_3Me_3(OTf)_2$]$^+$.

Synthesis of 6. $\mathbf{L}^{phen3}$ (200 mg, 0.256 mmol) was added to a CH_2Cl_2 solution of [Rh(nbd)$_2$]BF_4 (287 mg, 0.770 mmol) and stirred for 1 h. The precipitate in the reaction mixture was collected and the solid was washed with Et_2O and hexane, then dried under vacuum to yield a reddish brown solid (229 mg, 0.141 mmol, 55%). ^{1}H NMR (400 MHz, CD_3NO_2): δ 8.77 (d, J = 8.3 Hz, 3 H, H16), 8.65 (d, J = 8.5 Hz, 3 H, H9), 8.15–8.10 (m, 6 H, H12 + H13), 8.00 (d, J = 5.2 Hz, 3 H, H18), 7.96–7.92 (m, 3 H, H17), 7.68 (d, J = 8.3 Hz, 3 H, H8), 4.76 (12 H, -C=C*H* (nbd)), 4.20 (6 H, -C*H*-(nbd)), 3.26 (t, J = 8.3 Hz, 6 H, H5 or H6), 2.98 (t, J = 7.6 Hz, 6 H, H5 or H6), 2.58 (q, J = 7.3 Hz, 6 H, H3), 1.65 (6 H, -C*H*$_2$- (nbd)), 1.14 (t, J = 7.3 Hz, 9 H, H4). ^{13}C NMR (100 MHz, CD_3NO_2): δ 168.3 (s, C7) 149.5 (d, J_{CH} = 186 Hz, C18), 148.4 (s, C15), 148.0 (s, C11), 141.6 (d, J_{CH} = 169 Hz, C9), 141.5 (s, C1), 141.4 (d, J_{CH} = 161 Hz, C16), 136.1 (s, C2), 131.6 (s, C14), 130.1 (s, C10), 129.2 (d, J_{CH} = 166 Hz, C13), 128.1 (d, J_{CH} = 168 Hz, C12), 127.2 (d, J_{CH} = 168 Hz, C8), 126.6 (d, J_{CH} = 170 Hz, C17), 64.2 (t, J_{CH} = 153 Hz, *C*=*C*(nbd), 53.0 (d, J_{CH} = 155 Hz, -*C*H$_2$-(nbd)), 39.9 (t, J_{CH} = 128 Hz, C5 or C6), 29.9 (t, J_{CH} = 129 Hz, C5 or C6), 24.4 (t, J_{CH} = 126 Hz, C3), 16.3 (q, J_{CH} = 127 Hz, C4). ESI-MS (MeCN): m/z = 976.0 [$(\mathbf{L}^{phen3})Rh(nbd)$]$^+$, 1539.7 [$(\mathbf{L}^{phen3})Rh_3(nbd)_3(BF_4)_2$]$^+$.

Synthesis of 7. Complex **6** (200 mg, 0.133 mmol) was dissolved in CH_3NO_2 and 1 atm of CO gas was introduced into the reaction vessel after pumping at 0 °C, and the color of the solution turned from orange to yellow after stirring the reaction mixture at that temperature for 1 h. Et_2O was added to the solution and the resulting precipitate was redissolved into CH_3NO_2 and filtered through celite. The filtrate was concentrated, precipitation with Et_2O, and dried under vacuum to yield a reddish brown solid (168 mg, 0.110 mmol, 83%). ^{1}H NMR (400 MHz, CD_3NO_2): δ 9.26 (d, J = 4.9 Hz, 3 H, H18), 8.83 (d, J = 8.3 Hz, 3 H, H16), 8.75 (d, J = 8.5 Hz, 3 H, H9), 8.19–8.17 (m, 6 H, H12 + H13), 8.13–8.02 (m, 3 H, H17), 7.88 (d, J = 8.3 Hz, 3 H, H8), 3.63 (t, J = 7.6 Hz, 6 H, H5 or H6), 3.35 (t, J = 7.4 Hz, 6 H, H5 or H6), 2.62 (q, J = 7.4 Hz, 6 H, H3), 1.23 (t, J = 7.4 Hz, 9 H, H4). ^{13}C NMR (100 MHz, CD_3NO_2): δ 184.4 (d, $J_{Rh\text{-}C}$ = 72 Hz, *C*O), 155.6 (d, J_{CH} = 190 Hz, C18), 167.7 (s, C7), 148.7 (s, C15), 148.0 (s, C11), 143.2 (d, J_{CH} = 169 Hz, C9), 143.0 (d, J_{CH} = 161 Hz, C16), 141.9 (s, C1), 135.6 (s, C2), 132.4 (s, C14), 130.8 (s, C10), 129.5 (d, J_{CH} = 168 Hz, C13), 128.6 (d, J_{CH} = 168 Hz, C12), 127.6 (d, J_{CH} = 173 Hz, C8), 127.5 (d, J_{CH} = 169 Hz, C17), 46.2 (t, J_{CH} = 128 Hz, C5 or C6), 29.9 (t, J_{CH} = 129 Hz, C5 or C6), 24.3 (t, J_{CH} = 124 Hz, C3), 16.3 (q, J_{CH} = 127 Hz, C4). ESI-MS (MeCN): m/z = 939.9 [$(\mathbf{L}^{phen3})Rh(CO)_2$]$^+$, 1431.4 [$(\mathbf{L}^{phen3})Rh_3(CO)_6(BF_4)_2$]$^+$. IR ($CH_3NO_2$): ν_{CO} = 2096, 2034 cm^{-1}.

Synthesis of 8. A mixture of $\mathbf{L}^{pypz2}$ (104 mg, 0.22 mmol) and [Pd(cod)allyl]BF_4 (149 mg, 0.44 mmol) in CH_2Cl_2 (10 mL) was stirred at ambient temperature for 0.5 h. The volatiles were evaporated and the solid was precipitated by CH_2Cl_2–Et_2O to yield **8** as a white solid (122 mg, 0.13 mmol, 58% yield). ^{1}H NMR (200 MHz, CD_3NO_2): δ 8.79 (d, J = 4.9 Hz, 2 H, H17), 8.20 (t, J = 7.0 Hz, 2 H, H15), 8.09 (d, J = 7.6 Hz, 2 H, H14), 7.62 (t, J = 6.1 Hz, 2 H, H16), 7.42 (s, 1 H, H1), 7.36 (d, J = 2.7 Hz, 2 H, H10), 7.05 (d, J = 2.7 Hz, 2 H, H11), 6.05 (m, 2 H, C_3H_5), 5.68 (m, 4 H, H9), 4.82, 4.58 (d, J = 6.6 Hz, 4 H, C_3H_5-*syn*), 3.82, 3.54 (d, J = 12.4 Hz, 4 H, C_3H_5-*anti*), 2.75 (q, J = 7.6 Hz, 6 H, H5 + H7), 1.23 (t, J = 7.6 Hz, 6 H, H8), 1.12 (t, J = 7.6 Hz, 3 H, H6). ^{13}C NMR (100 MHz, CD_3NO_2): δ 154.8 (d, J_{CH} = 185 Hz, C17), 153.7 (s, C13), 151.6 (s, C3), 148.3 (s, C12), 146.2 (s, C2), 142.0 (d, J_{CH} = 169 Hz, C15), 134.3 (d, J_{CH} = 194 Hz, C10), 130.0 (d, J_{CH} = 157 Hz, C1), 128.1 (s, C4), 127.1 (d, J_{CH} = 177 Hz, C16), 123.1 (d, J_{CH} = 169 Hz, C14), 119.4 (d, J_{CH} = 166 Hz, C_3H_5), 105.9 (d, J_{CH} = 184 Hz, C11), 59.7, 66.6 (t, J_{CH} = 162, 152 Hz, C_3H_5), 52.5 (t, J_{CH} = 144 Hz, C9), 27.0 (t, J_{CH} = 128 Hz, C5), 23.9 (t, J_{CH} = 128 Hz, C7), 15.7 (q, J_{CH} = 128 Hz, C4), 15.3 (q, J_{CH} = 128 Hz, C4). ESI-MS (MeCN): m/z = 624.1 [$(\mathbf{L}^{pypz2})Pd(C_3H_5)$]$^+$, 858.4 [$(\mathbf{L}^{pypz2})Pd_2(C_3H_5)_2(BF_4)$]$^+$.

Synthesis of 9. [Rh(cod)$_2$]BF_4 (380 mg, 0.934 mmol) and $\mathbf{L}^{pypz2}$ (222 mg, 0.467 mmol) were dissolved in CH_3NO_2 (5 mL) and stirred at ambient temperature for 1 h. After the volatiles were removed under reduced pressure, the product was washed with Et_2O (20 mL × 3), and dried under vacuum to give **9** as an orange

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solid (450 mg, 0.420 mmol, 90% yield). ^{1}H NMR (400 MHz, CD_3NO_2): δ 8.14 (t, J = 7.6 Hz, 2 H, H15), 7.99 (d, J = 7.4 Hz, 2 H, H14), 7.83 (d, J = 5.5 Hz, 2 H, H17), 7.57 (t, J = 6.1 Hz, 2 H, H16), 7.40 (brs, 2 H, H10), 7.19 (s, 1 H, H1), 6.94 (d, J = 2.7 Hz, 2 H, H11), 5.26 (s, 4 H, H9), 4.97 (brs, 8 H, -C*H*=C*H*- (cod)), 2.65–2.08 (m, 22 H, H5 + H7 + -CH_2- (cod)), 1.23 (t, J = 7.4 Hz, 9 H, H6 + H8). ^{13}C NMR (100 MHz, CD_3NO_2): δ 156.4 (s, C13), 153.0 (s, C3), 148.9 (d, J_{CH} = 180 Hz, C17), 148.7 (s, C12), 146.3 (s, C2), 142.6 (d, J_{CH} = 169 Hz, C15), 136.2 (d, J_{CH} = 195 Hz, C10), 130.3 (d, J_{CH} = 157 Hz, C1), 128.1 (s, C4), 127.1 (d, J_{CH} = 172 Hz, C16), 123.6 (d, J_{CH} = 171 Hz, C14), 106.1 (d, J_{CH} = 184 Hz, C11), 84.8 (d, J_{CH} = 150 Hz, -*C*H=*C*H-), 50.2 (t, J_{CH} = 143 Hz, C9), 31.6 (t, J_{CH} = 130 Hz, -*C*H_2- (cod)), 27.2 (t, J_{CH} = 127 Hz, C5), 24.1 (t, J_{CH} = 128 Hz, C7), 16.1 (q, J_{CH} = 127 Hz, C8), 15.5 (q, J_{CH} = 128 Hz, C6). ESI-MS (MeCN): 687.7 [($\mathbf{L}^{pypz2}$)Rh(cod)]$^+$, 985.6 [($\mathbf{L}^{pypz2}$)Rh_2(cod)$_2$(BF_4)]$^+$. Elemental analysis data could not be obtained due to instability of the complex.

Synthesis of 10. A CH_3NO_2 solution (5 mL) of **9** (100 mg, 0.093 mmol) was degassed by a freeze–pump–thaw procedure and an atmospheric pressure of CO gas was introduced. Then the reaction mixture was cooled by an ice bath and stirred for 1 h. The resulting solution was precipitated by addition of Et_2O (20 mL). Then the precipitate was dissolved in CH_3NO_2, filtered through celite and reprecipitated, then dried under vacuum to afford **10** as a yellow solid (68 mg, 0.070 mmol, 75% yield). ^{1}H NMR (270 MHz, CD_3NO_2): δ 8.75 (d, J = 5.6 Hz, 2 H, H17), 8.28 (t, J = 7.7 Hz, 2 H, H15), 8.11 (d, J = 7.5 Hz, 2 H, H14), 7.69 (t, J = 5.6 Hz, 2 H, H16), 7.45 (s, 1 H, H1), 7.37 (d, J = 2.3 Hz, 2 H, H10), 7.06 (d, J = 2.7 Hz, 2 H, H11), 5.74 (s, 4 H, H9), 2.73 (q, J = 7.5 Hz, 6 H, H5 + H7), 1.23–1.14 (m, 9 H, H6 + H8). ^{13}C NMR (100 MHz, CD_3NO_2): δ 184.2 (d, $J_{Rh\text{-}C}$ = 70 Hz, *C*O), 156.3 (s, C13), 155.2 (d, J_{CH} = 185 Hz, C17), 152.1 (s, C3), 149.0 (s, C12), 146.6 (s, C2), 144.0 (d, J_{CH} = 170 Hz, C15), 136.5 (d, J_{CH} = 196 Hz, C10), 130.3 (d, J_{CH} = 158 Hz, C1), 128.1 (d, J_{CH} = 172 Hz, C16), 127.3 (C4), 124.0 (d, J_{CH} = 171 Hz, C14), 106.7 (d, J_{CH} = 186 Hz, C11), 52.9 (t, J_{CH} = 143 Hz, C9), 27.2 (t, J_{CH} = 128 Hz, C5), 24.2 (t, J_{CH} = 126 Hz, C7), 16.2 (q, J_{CH} = 127 Hz, C8), 15.5 (q, J_{CH} = 127 Hz, C6). IR (CH_3NO_2 solution) ν_{CO} = 2100, 2038 cm^{-1}. ESI-MS (MeCN): 635.5 [($\mathbf{L}^{pypz2}$)Rh(CO)$_2$]$^+$, 881.3 [($\mathbf{L}^{pypz2}$)Rh_2(CO)$_4$(BF_4)]$^+$. Anal. calcd for $C_{34}H_{32}B_2F_8N_6O_4Rh_2$ + Me_2CO: C, 43.31; H, 3.73; N, 8.19. Found: C, 42.94; H, 3.98; N 8.79%.

Synthesis of 11. $\mathbf{L}^{phen2}$ (100 mg, 0.174 mmol) was added to a CH_2Cl_2 solution of [(cod)Pd(C_3H_5)]BF_4 (120 mg, 0.348 mmol) and stirred at RT for 1 h. The resulting precipitate was collected by filtration and extracted with CH_3CN, and the volatile was removed under reduced pressure. The resulting solid was washed with Et_2O and hexane and drying under vacuum yielded a white solid (73 mg, 0.070 mmol, 40%). ^{1}H NMR (400 MHz, CD_3NO_2): δ 9.24 (d, J = 5.2 Hz, 3 H, H18), 8.81 (d, J = 8.3 Hz, 2 H, H16), 8.66 (d, J = 8.5 Hz, 2 H, H9), 8.12–8.16 (m, 4 H, H12 + H13), 8.04–8.00 (m, 2 H, H17), 7.75 (d, J = 8.5 Hz, 2 H, H8), 6.98 (s, 1 H, H22), 6.09 (m, J = 6.6 Hz, 2 H, allyl-*H*), 4.59 (d, J = 6.8 Hz, 4 H, allyl-*H*, *syn*), 3.76 (brs, allyl-*H*, *anti*), 3.60 (t, J = 7.3 Hz, 4 H, H5 or H6), 3.32 (t, J = 7.3 Hz, 4 H, H5 or H6), 2.60 (q, J = 7.2 Hz, 2 H, H3), 2.47 (q, J = 7.2 Hz, 4 H, H20), 1.15–1.09 (m, 9 H, H19 + H4). ^{13}C NMR (100 MHz, CD_3NO_2): δ 166.4 (s, C7), 155.4 (d, J_{CH} = 186 Hz, C18), 147.6 (s, C14), 147.2 (s, C11), 143.0 (s, C1), 142.4 (s, C21), 141.3 (d, J_{CH} = 166 Hz, C9), 141.2 (d, J_{CH} = 168 Hz, C16), 134.7 (s, C2), 132.1 (s, C15), 130.4 (s, C10), 129.1 (d, J_{CH} = 167 Hz, C13), 128.6 (d, J_{CH} = 157 Hz, C22), 128.1 (d, J_{CH} = 167 Hz, C12), 127.4 (d, J_{CH} = 171 Hz, C8), 127.2 (d, J_{CH} = 170 Hz, C17), 120.0 (t, J_{CH} = 165 Hz, C_3H_5), 66.7 (t, J_{CH} = 162 Hz, C_3H_5), 45.7 (t, J_{CH} = 128 Hz, C5 or C6), 29.4 (t, J_{CH} = 130 Hz, C5 or C6), 27.1 (t, J_{CH} = 127 Hz, C20), 23.8 (t, J_{CH} = 126 Hz, C3), 16.3 (q, J_{CH} = 127 Hz, C4), 16.1 (q, J_{CH} = 127 Hz, C19). ESI-MS (MeCN): m/z = 722.2 [($\mathbf{L}^{phen2}$)$Pd_2(C_3H_5)_2(BF_4)$]$^+$, 1190.8 [($\mathbf{L}^{phen2}$)$Pd_3(C_3H_5)_3(BF_4)_2$]$^+$.

Synthesis of 12. $\mathbf{L}^{phen2}$ (154 mg, 0.268 mmol) was added to a CH_2Cl_2 solution of [Rh(nbd)$_2$]BF_4 (200 mg, 0.536 mmol) and stirred at RT for 1 h. The resulting precipitate was collected by filtration, extracted with CH_3CN, and the volatile was removed under reduced pressure. The solid was washed with Et_2O and hexane and drying under vacuum yielded a reddish brown solid (131 mg, 0.126 mmol, 47%). ^{1}H NMR (400 MHz, CD_3NO_2): δ 8.75 (d, J = 8.0 Hz, 2 H, H16), 8.57 (d, J = 8.5 Hz, 2 H, H9), 8.11 (m, 4 H, H12 + H13), 8.00 (d, J = 5.1 Hz, 2 H, H18), 7.94–7.90 (m, 2 H, H17), 7.60 (d, J = 8.5 Hz, 2 H, H8), 6.97 (s, 1 H, H22), 4.73 (8 H, -C*H*=C*H*- (nbd)), 4.13 (4 H, -C*H*- (nbd)), 3.25 (t, J = 8.3 Hz, 4 H, H5 or H6), 2.96 (t, J = 7.6 Hz, 4 H, H5 or H6), 2.67 (q, J = 7.6 Hz, 4 H, H3), 2.44 (q, J = 7.6 Hz, 4 H, H20), 1.58 (4 H, -CH_2- (nbd)), 1.12 (t, J = 7.6 Hz, 9 H, H19 + H4). ^{13}C NMR (100 MHz, CD_3NO_2): δ 168.5 (s, C7), 149.3 (d, J_{CH} = 185 Hz, C18), 148.1 (s, C15), 147.8 (s, C11), 143.0 (s, C1), 142.3 (s, C21), 141.4 (d, J_{CH} = 170 Hz, C9), 141.2 (d, J_{CH} = 170 Hz, C16), 134.7 (s, C2), 131.4 (s, C14), 129.9 (s, C10), 129.2 (d, J_{CH} = 165 Hz, C13), 128.5 (d, J_{CH} = 154 Hz, C22), 127.9 (d, J_{CH} = 166 Hz, C12), 127.6 (d, J_{CH} = 168 Hz, C8), 126.6 (d, J_{CH} = 172 Hz, C17), 64.4 (t, J_{CH} = 153 Hz, -*C*H_2- (nbd)), 52.9 (d, J_{CH} = 155 Hz, -*C*H- (nbd)), 39.3 (t, J_{CH} = 129 Hz, C5 or C6), 29.5 (t, J_{CH} = 129 Hz, C5 or C6), 27.1 (t, J_{CH} = 127 Hz, C20), 23.9 (t, J_{CH} = 126 Hz, C3), 16.3 (q, J_{CH} = 127 Hz, C4), 16.0 (q, J_{CH} = 127 Hz, C19). ESI-MS (MeCN): m/z = 769.8 [($\mathbf{L}^{phen2}$)Rh(nbd)]$^+$, 1333.5 [($\mathbf{L}^{phen2}$)Rh_3(nbd)$_3$(BF_4)$_2$]$^+$.

Crystal structure determination

Data for compounds $\mathbf{L}^{pypz}$, **1**, and **2** were collected on a RIGAKU RAXIS-IV imaging plate area detector with a graphite monochromated Mo-Kα radiation source (λ = 0.71073 Å) at 213 K. In the reduction of data, Lorentz and polarization corrections were made.[19] The structures were solved by a combination of direct methods (SHELXS-86)[20] and Fourier synthesis (DIRDIF94).[21] All calculations were performed using the CrystalStructure[22] crystallographic software package except for refinement, which was performed using SHELXL-97.[20b] Unless otherwise stated, all non-hydrogen atoms were refined anisotropically, methyl hydrogen atoms were refined using riding models and other hydrogen atoms were fixed at the calculated positions. $\mathbf{L}^{pypz3}$: All the hydrogen atoms were refined isotropically and their positions were refined. **1**: All B and F atoms in the three independent BF_4 anions were refined isotropically. Two sets of disordered F atoms on the BF_4 anions were refined isotropically taking into account two components of three of four F atoms, respectively (occupancies refined as 0.5714 : 0.4286 for B(1)F_4, 0.5192 : 0.4808 for B(2)F_4, 0.6409 : 0.3591 for B(3)F_4). Three CH_3NO_2 molecules were included and they were refined isotropically. Hydrogen atoms on one of the nitromethane molecule were not included in the refinement. **2**: F atoms on the B(3) atom were refined isotropically taking into account two

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components of three of four F atoms (occupancies refined as 0.5245 : 0.4755). Three CH_3NO_2 molecules were included, one of the molecule was refined anisotropically and the rest were refined isotropically. The N atom in one of the isotropically refined CH_3NO_2 molecule is on the special position with its occupancy 0.5 and thus the occupancy of the whole molecule was fixed at 0.5. Hydrogen atoms attached to the disordered part were not included in the refinement.†

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