Hetero-bis(σ-aryl)dirhodium(III) caprolactamates. Electronic communication between aryl groups through dirhodium(III)†

Jian-Hua Xie, Lei Zhou, Conrad Lubek and Michael P. Doyle*

Received 5th December 2008, Accepted 2nd February 2009
First published as an Advance Article on the web 26th February 2009
DOI: 10.1039/b821592h

Fourteen hetero-bis(σ-aryl)dirhodium(III) caprolactamates that differ by the two aryl groups at the axial positions of dirhodium have been synthesized in good yield and characterized. Copper(II) catalyzed oxidation of dirhodium(II) caprolactamate at room temperature in the presence of two arylboronic acids results in a mixture of a hetero-bis(σ-aryl)dirhodium(III) caprolactamate and two homo-bis(σ-aryl)dirhodium(III) caprolactamates for each arylboronic acid combination. The UV-vis λ_{max} values for hetero-bisaryldirhodium(III) caprolactamates fall in between those for the corresponding homo-bisaryldirhodium(III) caprolactamates; electronic interaction between the two aryl groups occurs through dirhodium, but this transmission is probably indirect through the caprolactamate ligands rather than directly between rhodiums. The chemical shift for the carbon bound to Rh shows very limited dependence on the substituent from the aryl group on the adjacent Rh. Bisaryldirhodium(III) caprolactamates with electron-withdrawing substitutions have higher oxidation potentials than those with electron-donating substitutions. A plot of oxidation potentials *versus* the corresponding UV-visible absorption maxima for the bisaryldirhodium(III) caprolactamates shows a relationship between oxidation potentials and λ_{max} values. The electronic/electrochemical information obtained for hetero-bis(σ-aryl)dirhodium(III) caprolactamates suggests that communication between aryl substituents occurs.

Introduction

We have reported the first example of a bis-aryl dimetallic compound in a paddlewheel structure.[1] Formed from dirhodium(II) caprolactamate by oxidative coupling with sodium tetraphenylborate or arylboronic acids,[2] bisphenyldirhodium(III) carboxamidates are now well characterized.[3] They exhibit severe structural distortions of the phenyl groups from expected C–Rh–Rh–C linearity that is attributed to long range interactions between the electron-deficient rhodium and distal oxygen atoms,[3] and the Rh–Rh–O bond angles that are much less than the idealized perpendicular are in agreement with this interpretation. Consistent with experimental and computational results, these compounds do not have a Rh–Rh bond.[3] Fig. 1 gives structural representations for one of these bisphenyldirhodium(III) carboxamidates.

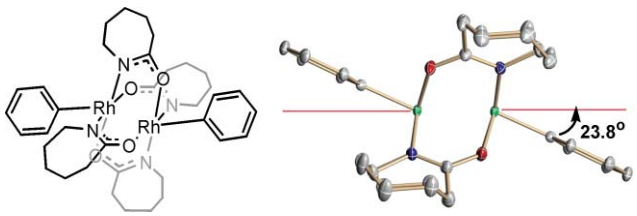
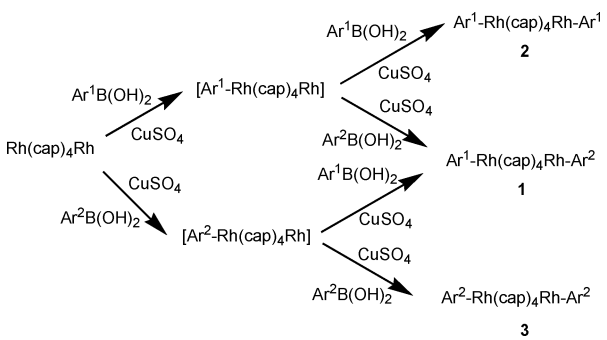


Fig. 1 Structural representations for bisphenyldirhodium(III) carprolactamate: (a) line drawing; (b) Ortep representation from CCDC# 615577.

Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland, 20742, USA. E-mail: mdoyle3@umd.edu; Fax: +13013142779; Tel: +13014051788

† Electronic supplementary information (ESI) available: NMR spectra. See DOI: 10.1039/b821592h

When we began these studies, and before our realization that bisphenyldirhodium(III) carboxamidates do not have a Rh–Rh bond, we considered that they may have potential as molecular wires. The elegant studies of Ren *et al.* with paddlewheel diruthenium σ-alkynyl compounds established them as conjugated organometallics suitably constructed to be molecular wires.[4] In these structures the acetylide moieties are collinear with the Ru–Ru vector and have characteristics of a molecular diode.[5] However, bisphenyldirhodium(III) carboxamidates have neither a Rh–Rh bond nor are the phenyl moieties collinear with the Rh–Rh vector. Given the potential synthetic ease for structural variations in aryl substituents in bisaryldirhodium(III) carboxamidates, we initiated the construction of these derivatives having two different aryl groups (Scheme 1). The challenges for this investigation were (1) delineating the potential electronic bias in coupling of the first and second aryl groups, (2) isolation of the individual



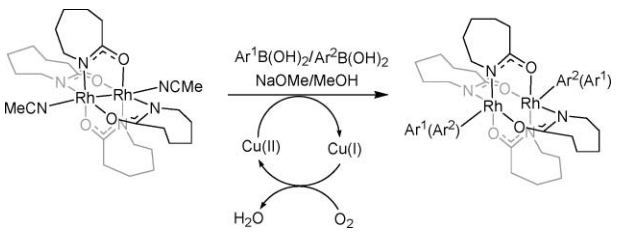
Scheme 1

isomers, and (3) characterization of the bisphenyldirhodium(III) carboxamidates with mixed aryl groups.

Results and discussion

Synthesis

Using the optimized reaction conditions for the synthesis of homo-bis(σ-aryl)dirhodium(III) caprolactamates,[2] hetero-bis(σ-aryl)dirhodium(III) caprolactamates were prepared by treatment of two different arylboronic acids with dirhodium(II) caprolactamate under oxidizing conditions. $Rh_2(cap)_4$ reacted smoothly under an atmosphere of air with a mixture of phenylboronic acid (2 equiv) and (4-methoxycarbonyl)phenylboronic acid (5 equiv) in the presence of 10 mol% $CuSO_4.5H_2O$ and 10 equiv. of NaOMe in methanol at room temperature for 24 h yielding a mixture of bis(σ-aryl)dirhodium(III) caprolactamates from which hetero-bis(σ-aryl)dirhodium(III) caprolactamate **1a** was isolated in 39% yield (Scheme 2). Homo-bis(σ-aryl)dirhodium(III) caprolactamates **2a** and **3a** were generated in 24% and 27% yields, respectively. Increasing the number of equivalents of phenylboronic acid led to higher yields of bis(σ-phenyl)dirhodium(III) caprolactamate **2a** (Fig. 2, $Ar^1 = C_6H_5$ and $Ar^2 = p$-$MeOOCC_6H_4$). Similarly, increasing the number of equivalents of (4-methoxycarbonyl)phenylboronic acid led to higher yields of bis(σ-4-methoxycarbonylphenyl)dirhodium(III) caprolactamate **3a**. In both cases, the yield of hetero bis(σ-aryl)dirhodium(III) caprolactamate **1a** decreased.



Scheme 2

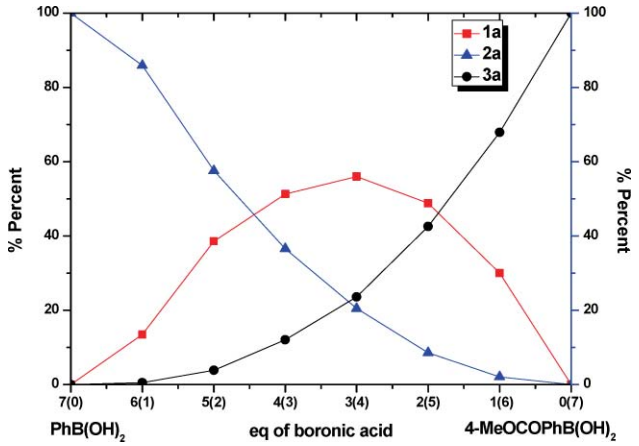
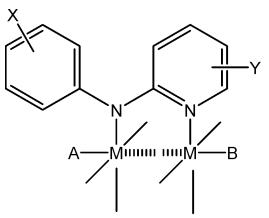


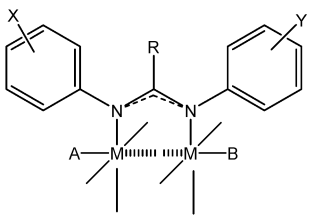
Fig. 2 $Rh_2(cap)_4(CH_3CN)_2$ with variable amounts of phenylboronic acid and (4-methoxycarbonyl)-phenylboronic acid in air, catalyzed by 10 mol% $CuSO_4$. Total molar equivalents of both arylboronic acids is 7.0 equiv.

Other combinations of arylboronic acids were treated under similar reaction conditions, and the results are reported in Table 1. As can be seen from these results, product ratios are not very sensitive to aryl substituents, although arylboronic acids having electron-withdrawing substituents are more reactive than those

Table 1 Synthesis of hetero-bis(σ-aryl)dirhodium(III) caprolactamates[a]



4



5

Comp.	Ar^1 (equiv)	Ar^2 (equiv), XC_6H_4 X =	**1**/∑**1–3** (%)[b]	**2**/∑**1–3** (%)[b]	**3**/∑**1–3** (%)[b]	Total yield (%)[c]
a	C_6H_5 (2)	4-MeOOC (5)	43	27	30	90
b	4-MeC_6H_4 (2)	4-MeOOC (5)	42	25	33	87
c	4-Ph-C_6H_4 (2)	4-MeOOC (5)	51	23	26	81
d	6-MeO-2-naphthyl (2)	4-MeOOC (5)	56	21	23	86
e	4-BrC_6H_4 (2)	4-MeOOC (5)	51	19	30	75
f	3-Thiopheneyl (2)	4-MeOOC (5)	40	30	30	77
g	4-$CF_3C_6H_4$ (5)	4-MeOOC (5)	55	20	25	85
h	3-$NO_2C_6H_4$ (5)	4-MeOOC (5)	48	29	23	65
i	C_6H_5 (2.5)	4-Me_2N (2.5)	40	22	38	78
j	C_6H_5 (2.5)	4-MeO (2.5)	46	14	40	65
k	C_6H_5 (2)	4-HCO (5)	48	20	32	91
k	C_6H_5 (2)	4-HCO (8)	45	8	47	91
l	4-$MeOC_6H_4$ (2)	4-HCO (5)	57	26	17	84
m	4-$Me_2NC_6H_4$ (2)	3-HCO (5)	50	10	40	79
n	4-$CF_3C_6H_4$ (5)	4-NO_2 (5)	40	35	25	60

[a] Reactions were performed at room temperature in 4:1 CH_2Cl_2/MeOH with 10 mol% $CuSO_4 \cdot 5H_2O$ and 10 equiv NaOMe with a reaction time of 12–24 h. [b] Relative yield of isolated products. [c] Isolated yield after column chromatography on silica gel.

with electron-donating substituents. Overall product yields were high for all arylboronic acid combinations.

UV-visible spectroscopy

The UV-visible spectra of the hetero-bis(σ-aryl)dirhodium(III) caprolactamates were obtained, and those for **1i**, **2i**, and **3i** are shown in Fig. 3. Focus was placed on the HOMO–LUMO transition that in all compounds occurs between 400 and 500 nm. This transition was determined by DFT methods to be from the δ* HOMO to an unoccupied mixed $RhRhC_{Ar}$ orbital in a compound whose Rh–Rh interaction is formally described as $\pi^4\delta^2\pi^{*4}\delta^{*2}$ so that the formal bond order for Rh–Rh is zero, suggesting that there should be no direct substituent influence on λ_{max}. Compared with the corresponding UV-vis spectra of homo-bis(σ-aryl)dirhodium (III) caprolactamates,[2] hetero-bis(σ-aryl)dirhodium(III) caprolactamates display their λ_{max} between those of the two homo-bis(σ-aryl)dirhodium(III) caprolactamates (Table 2). For example, the λ_{max} of compound **2i** and **3i** are at 430 nm and 485 nm, respectively, and λ_{max} for the corresponding hetero bis(σ-aryl)dirhodium (III) caprolactamate **1i** is at 440 nm. This result suggests electronic interaction between the two aryl groups through dirhodium, but this transmission is probably occurring indirectly through the caprolactamate ligands rather than directly through rhodium (Scheme 3, solid line or *via* dashed line). Similar indirect transmission of substituent effects in electronic spectra has been reported by Kadish, Bear *et al.* for tetrakis(2-anilinopyridinate) complexes of dirhodium in the +4, +5, and +6 oxidation states.[6]

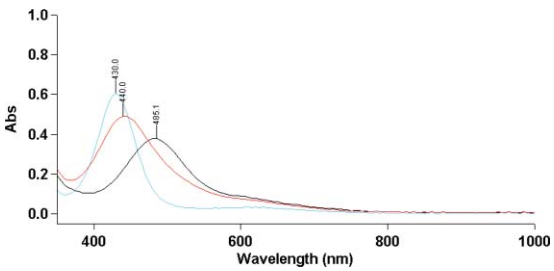
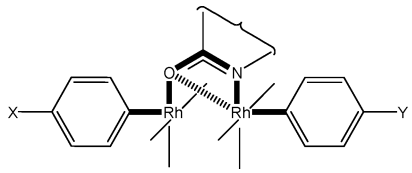


Fig. 3 Uv-vis spectra of compound **1i**, **2i** and **3i** (red line for compound **1i**, green line for compound **2i** and gray line for compound **3i**, 1.0×10^{-4} mmol mL^{-1}).



Scheme 3

^{13}C chemical shift

The ^{13}C chemical shift of the carbon directly attached to rhodium is dependent on the substituent on the phenyl group. With electron-withdrawing substitutions higher chemical shifts are observed; lower chemical shifts are found when substituents are electron donating (Table 3). As can be seen from the series **1a** through **1h** the chemical shift for the carbon bound to Rh in $4\text{-}MeO_2CC_6H_4$ shows very limited dependence on the substituent from the distant aryl group. The $J_{Rh\text{-}C}$ coupling constants from mononuclear phenylrhodium(III) compounds are much lower than those reported here for bis(σ-aryl)dirhodium(III).[7]

Electrochemistry

Finally, cyclic voltammetry data was obtained for this set of hetero-bis(σ-aryl)dirhodium(III) caprolactamates (Table 4). Cyclic voltammetry analyses were carried out by dissolving the respective hetero-bis(σ-aryl)dirhodium(III) caprolactamates in CH_2Cl_2 solution under nitrogen with 0.10 M NBu_4PF_6 as the supporting electrolyte. Electrochemical oxidation/reduction was obtained on Pt (working/auxiliary) and Ag/AgCl reference electrodes and referenced to ferrocene$^{(0,+)}$. All complexes exhibited reversible oxidation (Rh^{6+}/Rh^{7+}) waves with the reduction peak separated from the oxidation peak by 100–140 mV except for the two complexes having the dimethylamino group (**2i** and **2m**), which exhibited multiple redox peaks, presumably associated with that easily oxidized functional group. As had been previously reported for bisphenyldirhodium(III) carboxamidates,[3] an additional irreversible redox couple, attributed to Rh^{5+}/Rh^{6+}, could be observed near the reduction limit of the solvent. Complexes with electron-withdrawing substitutions have higher oxidation potentials than those with electron-donating substitutions. The

Table 2 UV-vis data of hetero bis(σ-aryl)dirhodium(III) caprolactamates

Compound	Ar^1	Ar^2, XC_6H_4 X =	λ_{max}/nm ($\varepsilon \times 10^{-3}$ M^{-1} cm^{-1})		
			1 (Ar^1Ar^2)	**2** (Ar^1Ar^1)	**3** (Ar^2Ar^2)
a	C_6H_5	$4\text{-}MeOOCC_6H_4$	430 (6.2)	430(4.5)	425(8.2)
b	$4\text{-}MeC_6H_4$	$4\text{-}MeOOCC_6H_4$	430 (7.7)	440(8.1)	425(8.2)
c	$4\text{-}Ph\text{-}C_6H_4$	$4\text{-}MeOOCC_6H_4$	430 (7.2)	440(1.3)	425(8.2)
d	6-MeO-2-naphthyl	$4\text{-}MeOOCC_6H_4$	435 (6.1)	455(6.2)	425(8.2)
e	$4\text{-}BrC_6H_4$	$4\text{-}MeOOCC_6H_4$	430 (6.7)	432(8.0)	425(8.2)
f	3-Thiopheneyl	$4\text{-}MeOOCC_6H_4$	430 (5.3)	457(5.9)	425(8.2)
g	$4\text{-}CF_3C_6H_4$	$4\text{-}MeOOCC_6H_4$	425 (5.4)	420(4.2)	425(8.2)
h	$3\text{-}NO_2C_6H_4$	$4\text{-}MeOOCC_6H_4$	425 (6.6)	423(6.4)	425(8.2)
i	C_6H_5	$4\text{-}Me_2NC_6H_4$	440 (4.0)	430(4.5)	485(3.1)
j	C_6H_5	$4\text{-}MeOC_6H_4$	440 (4.8)	430(4.5)	452(6.2)
k	C_6H_5	$4\text{-}HCOC_6H_4$	425 (5.4)	430(4.5)	422(7.9)
l	$4\text{-}MeOC_6H_4$	$4\text{-}HCOC_6H_4$	435 (5.2)	452(6.2)	422(7.9)
m	$4\text{-}Me_2NC_6H_4$	$3\text{-}HCOC_6H_4$	430 (4.1)	485(3.1)	425(4.1)
n	$4\text{-}CF_3C_6H_4$	$4\text{-}NO_2C_6H_4$	420 (8.9)	420(4.2)	415(8.9)

Table 3 ^{13}C Chemical shift of Rh–C of hetero bis(σ-aryl)dirhodium(III) caprolactamates

Compound	**1**: (Ar^1Ar^2), δ, ppm (multiplicity, *J*, Hz)	**2**: Ar^1, δ, ppm (multiplicity, *J*, Hz)	**3**: Ar^2, XC_6H_4, X =, δ, ppm (multiplicity, *J*, Hz)
a	146.9 (d, 36.1); 157.9 (d, 39.0)	C_6H_5, 147.8 (d, 37.1)	4-MeO_2C, 157.6 (d, 37.0)
b	142.3 (d, 36.9); 158.2 (d, 37.2)	4-MeC_6H_4, 142.8 (d, 37.0)	4-MeO_2C, 157.6 (d, 37.0)
c	146.5 (d, 36.7); 157.9 (d, 38.0)	4-PhC_6H_4, 146.6 (d, 37.0)	4-MeO_2C, 157.6 (d, 37.0)
d	140.4 (d, 36.8); 157.9 (d, 36.2)	6-MeO-2-naphthyl, 140.4 (d, 36.8)	4-MeO_2C, 157.6 (d, 37.0)
e	144.8 (d, 38.2); 157.3 (d, 37.1)	4-BrC_6H_4, 144.8 (d, 38.2)	4-MeO_2C, 157.6 (d, 37.0)
f	128.0 (d, 42.8); 156.7 (d, 36.7)	3-Thiophenyl, 128.0 (d, 42.8)	4-MeO_2C, 157.6 (d, 37.0)
g	153.7 (d, 29.2); 157.6 (d, 37.8)	4-$CF_3C_6H_4$,NA	4-MeO_2C, 157.6 (d, 37.0)
h	146.4 (d, 39.1); 156.6 (d, 36.7)	3-$NO_2C_6H_4$, 146.4 (d, 39.1)	4-MeO_2C, 157.6 (d, 37.0)
j	147.3 (d, 37.0); 131.2 (d, 37.0)	C_6H_4, 147.8 (d, 37.1)	4-Me_2N, 131.4 (d, 37.6)
k	147.8 (d, 37.1); 163.4 (d, 33.8)	C_6H_4, 146.8 (d, 36.3)	4-HCO, 162.3 (d, 37.0)
l	134.0 (d, 37.5); 162.5 (d, 33.9)	4-$MeOC_6H_4$, 134.2 (d, 38.7)	4-HCO, 161.5 (d, 37.0)
n	130.7 (d, 37.8); 147.9 (d, 39.3)	4-$Me_2NC_6H_4$, 130.7 (d, 37.8)	3-HCO, 148.3 (d, *J* = 37.0)

Table 4 CV data for $Ar^1Ar^2Rh_2cap_4$

Compound	Ar^1	Ar^2 XC_6H_4, X =	E_{pa}/V[a]	E_{pc}/V	$E_{1/2}$/V
a	C_6H_5	4-MeOOC	0.980	0.841	0.9105
b	4-MeC_6H_4	4-MeOOC	0.973	0.838	0.9055
c	4-Ph-C_6H_4	4-MeOOC	1.002	0.864	0.933
d	6-MeO-2-naphthyl	4-MeOOC	1.009	0.852	0.9305
e	4-BrC_6H_4	4-MeOOC	1.031	0.898	0.9645
f	3-Thiopheneyl	4-MeOOC	1.031	0.897	0.964
g	4-$CF_3C_6H_4$	4-MeOOC	1.069	0.937	1.003
h	3-$NO_2C_6H_4$	4-MeOOC	1.102	0.979	1.0405
i	C_6H_5	4-Me_2N	[b]	[b]	[b]
j	C_6H_5	4-MeO	0.893	0.776	0.8345
k	C_6H_5	4-HCO	1.005	0.896	0.9505
l	4-$MeOC_6H_4$	4-HCO	0.982	0.877	0.9295
m	4-$Me_2NC_6H_4$	3-HCO	[b]	[b]	[b]
n	4-$CF_3C_6H_4$	4-NO_2	1.124	1.016	1.07

[a] Pt (working and auxiliary) and Ag/AgCl reference electrodes, CH_2Cl_2, Bu_4NPF_6. [b] Multiple irreversible redox peaks were found.

opposite trend is found in the UV-visible data of the hetero-bis(σ-aryl)dirhodium(III) caprolactamates in that complexes with electron-withdrawing substituents have lower absorption maxima than those with electron-donating substituents. A plot of half-wave potentials *versus* the corresponding UV-visible absorption maxima for the hetero-bis(σ-aryl)dirhodium(III) caprolactamates (Fig. 4)

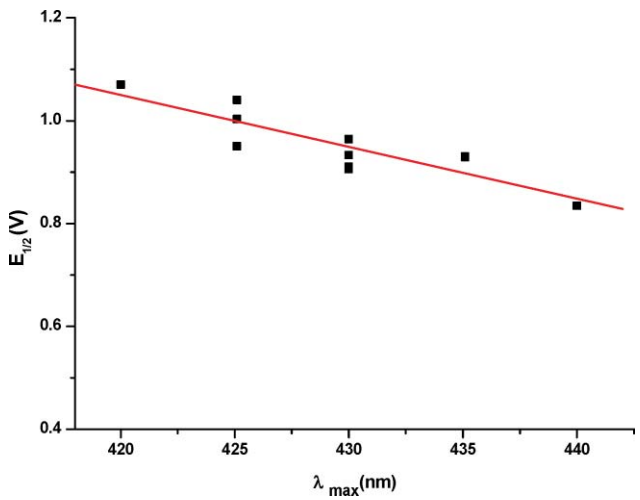


Fig. 4 Plot of $E_{1/2}$/V *vs.* λ_{max}/nm for $Ar^1Ar^2Rh_2cap_4$. (R^2 = 0.7508; slope = –0.0101).

Table 5 CV and UV-vis data for $Ar_2Rh_2cap_4$

Ar =	E_{pa}/V[a]	E_{pc}/V	$E_{1/2}$/V	λ_{max}/nm
3-$HCOC_6H_4$	1.017	0.946	0.9815	425.1
4-BrC_6H_4	0.992	0.919	0.9555	430
4-$HCOC_6H_4$	1.057	0.986	1.0215	425.1
4-$MeOC_6H_4$	0.855	0.781	0.818	449.9
4-(BocNH)C_6H_4	0.877	0.797	0.837	449.9
4-$MeOOCC_6H_4$	1.038	0.926	0.982	425.1
4-$CF_3C_6H_4$	1.064	0.962	1.013	420
4-MeC_6H_4	0.864	0.760	0.812	440
4-PhC_6H_4	0.921	0.817	0.869	440

[a] Pt (working and auxiliary) and Ag/AgCl reference electrodes, CH_2Cl_2, Bu_4NPF_6.

defines the relationship between oxidation potentials and λ_{max} values. The trend shows that the higher the half-wave potential, the lower UV-visible absorption maximum. Similar data was obtained for homo-bis(σ-aryl)dirhodium(III) caprolactamates (Table 5 and Fig. 5).

Noteworthy in Tables 4 and 5 is the distinctive influence of λ_{max} for aryl substituents on the half-wave potential. The results in Table 4 from $Ar^1Ar^2Rh_2cap_4$ for Ar^2 = 4-$MeOOCC_6H_4$ (**a-h**) show correlation of $E_{\frac{1}{2}}$ with those in Table 5 for homo-bis(σ-aryl)dirhodium(III) caprolactamates. The oxidized bis-aryldirhodium(III,IV) caprolactamates are obviously stable, but

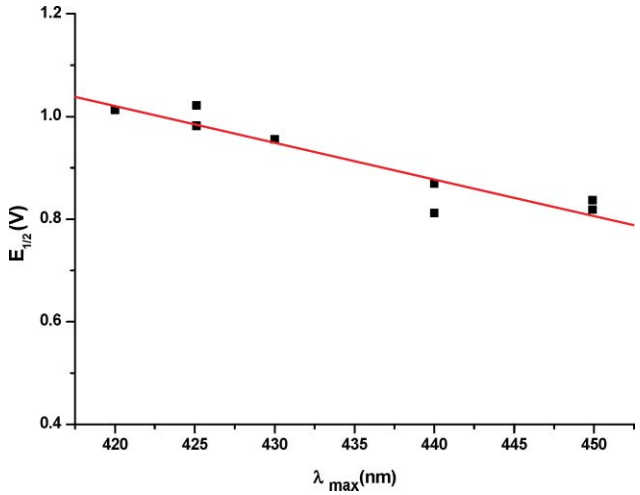


Fig. 5 Plot of $E_{1/2}$/V *vs.* λ_{max}/nm for $Ar_2Rh_2cap_4$. ($R^2 = 0.8835$; slope = –0.0071).

the corresponding bisaryldirhodium(II,III) caprolactamates are not. However, we have not yet been able to chemically oxidize bis(σ-aryl)dirhodium(III) caprolactamates (ferricinium salts, nitrosonium salts).

The influence of aryl substituents on half-wave potentials has allowed the establishment of a linear free energy relationship between $E_{1/2}$ for homo-bis(σ-aryl)dirhodium(III) caprolactamates and σ (Fig. 6) through the Hammett equation.[8] Linear correlation with published σ-values (σ_p and σ_m)[9] is observed with $R^2 = 0.9866$ and a slope (reaction constant) of +0.306 (ρ). To investigate if significant conjugation occurs between the phenyl substituent and the dirhodium core, plots with σ^+ and σ^- were also attempted, but each had low correlation coefficients. The correlation exhibited in Fig. 6 is in good agreement with the electron-donating-withdrawing properties of phenyl substituents. Substituent effects with $E_{1/2}$ values in dimetallic systems have been previously reported and discussed,[10] and similar correlations in iron-phenylacetylide compounds have also been examined.[11]

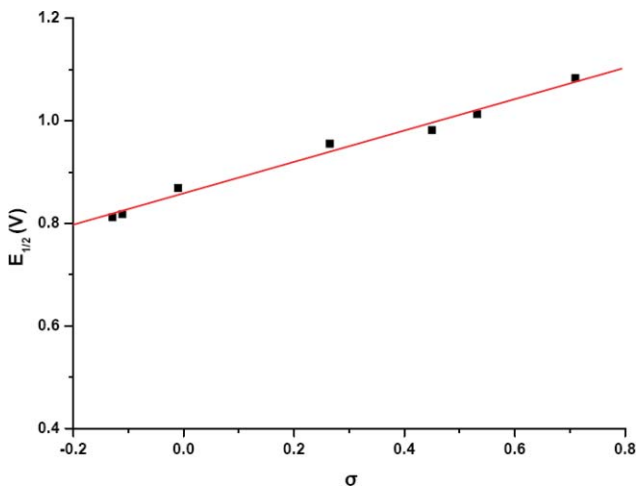
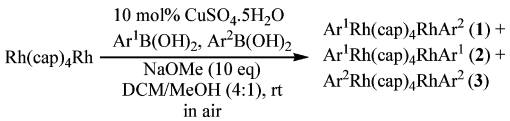


Fig. 6 Plot of $E_{1/2}$/V *vs.* σ for $Ar_2Rh_2cap_4$.

Conclusions

Electrochemical and spectroscopic information have been abundantly provided for selected dirhodium[12] and diruthenium[13] complexes. Substituent effects from anilinopyridinate (**4**)[5,14] and diarylformamidinate (**5**)[15] complexes have been reported, and linear free energy relationships have been provided. However, the alignment of aryl rings in these complexes is inherently different from that of bisaryldirhodium(III) carboxamidates, and direct comparisons cannot be made. Indeed, we know of no comparable dimetallic system from which similar data could be extracted. Bisaryldirhodium(III) carboxamidates provide a unique opportunity to probe substituent effects that are transmitted from remote positions directly to rhodium. That the values for λ_{max} and $E_{1/2}$ in hetero-bis(σ-aryl)dirhodium(III) caprolactamates fall between those for homo-bis(σ-aryl)dirhodium(III) caprolactamates suggests that communication between aryl substituents does occur. Without a Rh–Rh bond the effects are localized on an individual rhodium and passed onto the adjacent rhodium through carboxamidate ligands (Scheme 3).



Experimental

General

All reagents and solvents were used without further purification. Yields reported are those obtained after chromatography on silica gel (SiliCycle, 60A, 40–63 mesh), unless otherwise noted. The preparation of dirhodium(II) caprolactamate $[Rh_2(cap)_4(CH_3CN)_2]$ has been previously described.[16] ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker DRX-400 NMR as solutions in $CDCl_3$ unless otherwise noted. Chemical shifts are reported in parts per million (ppm, δ) downfield from Me_4Si (TMS); coupling constants are reported in Hertz (Hz). UV-visible spectra were obtained on a Varian Cary 50 spectrophotometer using a xenon lash lamp. IR spectra were recorded on a JASCO FT/IR 4100 spectrometer. Mass spectra were recorded at high resolution with either a VG Micromass 70/70H or VG ZAB-E spectrometer. Electrochemical measurements were performed in freshly distilled CH_2Cl_2 (N_2 degassed) with a CHI 610c instrument. A three-electrode cell was used (Pt working and auxiliary electrodes, Ag/AgCl reference electrode). The ferrocenium/ferrocene couple was observed at 0.487 V (*vs.* Ag/AgCl) under the experimental conditions. Scans were run at 100 mV s^{-1} under a nitrogen atmosphere. Solutions were 0.5–1.0 mM of analyte in 10 mL of CH_2Cl_2 of 0.1 M Bu_4NPF_6 as the supporting electrolyte. Nitrogen gas was bubbled through the solution for 10 min before each set of measurements and was passed continuously over the surface of the solution during the measurements.

General procedure

$CuSO_4{\cdot}5H_2O$ (3.0 mg, 12 μmol) was dissolved in 4 mL MeOH, and this solution was added to the mixture of $Rh_2(cap)_4(MeCN)_2$

(88.4 mg, 0.12 mmol), NaOMe (64.8 mg, 1.2 mmol) and arylboronic acids (0.24–0.96 mmol) in 16 mL CH_2Cl_2. The generated purple reaction solution was stirred at room temperature for 12–24 hrs to complete the reaction (determined by TLC, CH_2Cl_2 or CH_2Cl_2/acetone = 98:2). The solvents were then removed under reduced pressure, and the green or yellow solid residue was purified by chromatography on silica gel using CH_2Cl_2 or CH_2Cl_2/acetone as the eluent. The products were identified spectroscopically.

***trans*-{σ-Phenyl-σ-(4-methoxycarbonylphenyl)}-*tetrakis*-μ-(caprolactamato)dirhodium(III) (1a).** Green solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.50 (comp, 2H), 7.11 (comp, 3H), 3.91 (s, 3H), 3.02–2.929 (comp, 8H), 2.51–2.32 (comp, 8H), 1.81 (comp, 4H), 1.68–1.38 (comp, 20H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.3, 184.0, 168.2, 157.9 (d, J = 39.0 Hz), 146.9 (d, J = 36.1 Hz), 137.1, 136.8, 126.8, 126.5, 126.2, 124.4, 51.6, 51.5, 39.0, 38.9, 30.7, 29.9, 29.8, 24.4; UV-visible (CH_2Cl_2): λ_{max} (ε M^{-1} cm^{-1}) = 425 (6200); HRMS (ESI): Calcd for $C_{38}H_{53}N_4O_6Rh_2$ ([M + H]$^+$): 867.2075; Found: 867.2078.

***trans*-{σ-(4-Methylphenyl)-σ-(4-methoxycarbonylphenyl)}-*tetrakis*-μ-(caprolactamato)-dirhodium(III) (1b).** Green solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 8.8 Hz, 2H), 7.68 (d, J = 8.8 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 6.95 (d, J = 8.4 Hz, 2H), 3.91 (s, 3H), 3.06–2.90 (comp, 8H), 2.40 (comp, 8H), 1.80 (comp, 4H), 1.65–1.38 (comp, 20H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.2, 183.9, 168.2, 158.2 (d, J = 37.2 Hz), 142.3 (d, J = 36.9 Hz), 137.1, 136.4, 133.7, 127.5, 126.7, 126.1, 51.8, 51.7, 51.6, 38.9, 38.8, 30.7, 29.9, 29.7, 29.7, 24.4, 20.7; UV-visible (CH_2Cl_2): λ_{max} (ε M^{-1} cm^{-1}) = 430 (7660); HRMS (ESI): Calcd for $C_{39}H_{54}N_4O_6Rh_2$ (M^+): 880.2153; Found: 880.2168.

***trans*-{σ-(4-Phenylphenyl)-σ-(4-methoxycarbonylphenyl)}-*tetrakis*-μ-(caprolactamato)-dirhodium(III) (1c).** Green solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.8 Hz, 2H), 7.65 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.30 (t, J = 7.6 Hz, 1H), 3.91 (s, 3H), 3.12–2.4 (comp, 8H), 2.44 (comp, 8H), 1.82 (comp, 4H), 1.68–1.38 (comp, 20H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.3, 184.1, 168.2, 157.9 (d, J = 38.0 Hz), 146.5 (d, J = 36.7 Hz), 141.6, 137.5, 137.1, 137.0, 128.6, 127.1, 126.8, 126.5, 126.2, 125.2, 51.8, 51.7, 39.0, 38.9, 30.8, 29.9, 29.8, 24.4; UV-visible (CH_2Cl_2): λ_{max} (ε M^{-1} cm^{-1}) = 435 (7200); HRMS (ESI): Calcd for $C_{44}H_{57}N_4O_6Rh_2$ ([M + H]$^+$): 943.2388; Found: 943.2392.

***trans*-{σ-(6-Methoxynaphthalen-2-yl)-σ-(4-methoxycarbonylphenyl)}-*tetrakis*-μ-(caprolactamato)-dirhodium(III) (1d).** Green solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (s, 1H), 7.77 (d, J = 8.8 Hz, 2H), 7.74–7.62 (m, 4H), 7.51 (d, J = 8.8 Hz, 1H), 7.18 (d, J = 2.4 Hz, 1H), 7.08 (dd, J = 8.8, 2.4 Hz, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 3.06–2.90 (comp, 8H), 2.45 (comp, 8H), 1.83 (comp, 4H), 1.70–1.42 (comp, 20H); ^{13}C NMR ($CDCl_3$): δ 184.3, 184.1, 168.2, 157.9 (J = 36.2 Hz), 156.6, 140.4 (J = 36.8 Hz), 137.1, 135.6, 134.3, 132.9, 128.8, 128.5, 126.8, 126.6, 123.9, 117.4, 105.6, 55.3, 51.8, 51.7, 51.6, 39.0, 38.9, 30.8, 29.9, 29.8, 24.4; UV-visible (CH_2Cl_2): λ_{max} (ε M^{-1} cm^{-1}) = 435 (6068); HRMS (ESI): Calcd for $C_{43}H_{57}N_4O_6Rh_2$ ([M + H]$^+$): 947.2337; Found: 947.2323.

***trans*-{σ-(4-Bromophenyl)-σ-(4-methoxycarbonylphenyl)}-*tetrakis*-μ-(caprolactamato)-dirhodium(III) (1e).** Green solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 8.8 Hz, 2H), 7.65 (d, J = 8.8 Hz, 2H), 7.38 (d, J = 8.8 Hz, 2H), 7.25 (d, J = 8.8 Hz, 2H), 3.91 (s, 3H), 2.98–2.89 (comp, 8H), 2.48–2.34 (comp, 8H), 1.82 (comp, 4H), 1.62–1.37 (comp, 20H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.2, 168.1, 157.3 (d, J = 37.1 Hz), 144.8 (d, J = 38.2 Hz), 138.3, 137.0, 132.3, 129.6, 126.4, 119.0, 117.2, 51.8, 51.6, 51.5, 38.9, 30.7, 29.8, 24.3; UV-visible (CH_2Cl_2): λ_{max} (ε M^{-1} cm^{-1}) = 425 (6670); HRMS (ESI): Calcd for $C_{38}H_{51}N_4O_6Rh_2$ (M^+): 944.1102; Found: 944.1069.

***trans*-{σ-(3-Thienyl)-σ-(4-methoxycarbonylphenyl)}-*tetrakis*-μ-(caprolactamato)dirhodium(III) (1f).** Green solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 4.8 Hz, 1H), 7.32 (dd, J = 4.8, 2.8 Hz, 1H), 7.08 (d, J = 2.8 Hz, 1H), 3.90 (s, 3H), 3.10–2.89 (comp, 8H), 2.50–2.32 (comp, 8H), 1.82 (comp, 4H), 1.65–1.38 (comp, 20H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.1, 184.0, 168.1, 156.7 (d, J = 36.7 Hz), 137.0, 132.9, 128.0 (d, J = 42.8 Hz), 126.8, 126.4, 120.1, 119.3, 51.8, 51.7, 51.6, 39.0, 38.8, 30.7, 29.9, 29.7, 24.4; UV-visible (CH_2Cl_2): λ_{max} (ε M^{-1} cm^{-1}) = 435 (5304); HRMS (ESI): Calcd for $C_{36}H_{50}N_4O_6Rh_2S$ (M^+): 872.1561; Found: 872.1512.

***trans*-{σ-(4-Trifluoromethylphenyl)-σ-(4-methoxycarbonylphenyl)}-*tetrakis*-μ-(caprolactamato)-dirhodium(III) (1g).** Green solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 8.8 Hz, 2H), 7.68 (d, J = 8.8 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 6.95 (d, J = 8.4 Hz, 2H), 3.91 (s, 3H), 3.06–2.90 (comp, 8H), 2.40 (comp, 8H), 1.80 (comp, 4H), 1.65–1.38 (comp, 20H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 184.2, 184.1, 167.7, 157.6 (d, J = 37.8 Hz), 153.7 (d, J = 29.2 Hz), 137.2, 137.0, 126.9, 126.6, 126.5, 122.2 (q, J = 3.2 Hz), 115.5, 51.7, 51.6, 38.7, 30.6, 29.7, 24.3; UV-visible (CH_2Cl_2): λ_{max} (ε M^{-1} cm^{-1}) = 420 (5361); HRMS (ESI): Calcd for $C_{39}H_{52}F_3N_4O_6Rh_2$ ([M + H]$^+$): 935.1949; Found: 935.1964.

***trans*-{σ-(3-Nitrophenyl)-σ-(4-methoxycarbonylphenyl)}-*tetrakis*-μ-(caprolactamato)dirhodium(III) (1h).** Green solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (s, 1H), 8.00 (dd, J = 8.0, 1.6 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.4 Hz, 2H), 7.25 (t, J = 8.0 Hz, 1H), 3.92 (s, 3H), 3.02–2.87 (comp, 8H), 2.51–2.37 (comp, 8H), 1.81 (comp, 4H), 1.71–1.38 (comp, 20H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.6, 184.4, 168.2, 156.6 (d, J = 36.7 Hz), 146.4 (d, J = 39.1 Hz), 145.6, 143.6, 136.8, 131.3, 130.0, 127.0, 126.6, 126.0, 122.0, 119.7, 15.2, 110.6, 51.9, 51.8, 51.7, 39.0, 38.9, 30.7, 29.7, 29.6, 24.3; UV-visible (CH_2Cl_2): λ_{max} (ε M^{-1} cm^{-1}) = 425 (6642); HRMS (ESI): Calcd for $C_{38}H_{52}N_5O_8Rh_2$ ([M + H]$^+$): 912.1926; Found: 912.1898.

***trans*-{σ-(4-*N*,*N*-Dimethylaminophenyl)-σ-phenyl}-*tetrakis*-μ-(caprolactamato)dirhodium(III) (1i).** Green solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (comp, 2H), 7.33 (d, J = 8.8 Hz, 2H), 7.11 (comp, 3H), 6.70 (d, J = 8.8 Hz, 2H), 3.13–2.89 (comp, 8H), 2.95 (s, 6H), 2.54–2.32 (comp, 8H), 1.81 (comp, 4H), 1.68–1.38 (comp, 20H); ^{13}C NMR ($CDCl_3$): δ 183.8, 183.7, 149.0, 147.3 (d, J = 37.0 Hz), 137.1, 136.3, 131.2 (d, J = 37.0 Hz), 127.8, 126.3, 124, 114.0, 112.8, 51.6, 41.5, 39.0, 30.9, 30.8, 30.0, 24.5, 24.4; UV-visible (CH_2Cl_2): λ_{max} (ε M^{-1} cm^{-1}) = 440 (4960); HRMS (ESI): Calcd for $C_{38}H_{56}N_5O_4Rh_2$ ([M + H]$^+$): 852.2442; Found: 852.2422.

***trans*-{σ-(4-Methoxyphenyl)-σ-phenyl}-*tetrakis*-μ-(caprolactamato)dirhodium(III) (1j).** Green solid; ^{1}H NMR (400 MHz,

$CDCl_3$): δ 7.51 (comp, 2H), 7.39 (d, J = 8.8 Hz, 2H), 7.10 (comp, 3H), 6.80(d, J = 8.8 Hz, 2H), 3.84 (s, 3H), 3.08–2.91 (comp, 8H), 2.48–2.35 (comp, 8H), 1.80 (comp, 4H), 1.67–1.36 (comp, 20H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.0, 183.9, 157.8, 147.0 (d, J = 36.6 Hz), 137.0, 136.6, 134.9 (d, J = 39.1 Hz), 126.4, 124.1, 116.0, 114.8, 112.5, 55.8, 55.5, 51.6, 51.5, 38.9, 30.8, 29.9, 24.4; UV-visible (CH_2Cl_2): λ_{max} (ε M^{-1} cm^{-1}) = 440 (4750); HRMS (ESI): Calcd for $C_{37}H_{52}N_4O_5Rh_2$ (M^+): 838.2048; Found: 838.2057.

***trans*-{σ-(4-Formylphenyl)-σ-phenyl}-*tetrakis*-μ-(caprolactamato)dirhodium(III) (1k).** Green solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.03 (s, 1H), 7.84 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8 Hz, 2H), 7.53–7.50 (comp, 2H), 7.15–7.13 (comp, 3H), 3.06–2.96 (comp, 8H), 2.45–2.40 (comp, 8H), 1.83–1.79 (comp, 4H), 1.63–1.39 (comp, 20H); ^{13}C NMR (100 MHz, $CDCl_3$/MeOD, 4:1): δ 192.7, 184.4, 184.0, 137.8, 136.8, 133.5, 126.7, 126.6, 124.5, 51.7, 51.5, 39.0, 38.9, 30.7, 29.9, 29.7, 24.4; UV-visible (CH_2Cl_2): λ_{max} (ε M^{-1} cm^{-1}) nm = 425 (5400); HRMS (ESI): Calcd for $C_{37}H_{50}N_4O_5Rh_2$ (M^+): 836.1891; Found: 836.1915. HRMS (ESI): Calcd for $C_{37}H_{50}N_4O_5Rh_2$ (M^+): 836.1891; Found: 836.1915. $C_{37}H_{51}N_4O_5Rh_2$ ([M + H]$^+$): 837.1970; Found: 836.1979.

***trans*-{σ-(4-Methoxyphenyl)-σ-(4-formylphenyl)}-*tetrakis*-μ-(caprolactamato)dirhodium(III) caprolactamate (1l).** Green solid. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 10.00 (s, 1H), 7.79 (d, J = 8.0 Hz, 2H), 7.57 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 6.79 (d, J = 8.0 Hz, 2H), 3.83 (s, 3H), 2.99 (comp, 8H), 2.47–2.36 (comp, 8H), 1.82 (comp, 4H), 1.63–1.39 (comp, 20H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 192.2, 184.1, 183.7, 162.5 (d, J = 33.9 Hz), 158.0, 137.9, 136.5, 134.0 (d, J = 37.5 Hz), 133.5, 1130.1, 128.0, 126.3, 112.3, 55.4, 51.7, 51.4, 38.7, 38.6, 30.7, 29.9, 29.7, 24.3; UV-visible (CH_2Cl_2): λ_{max} (ε M^{-1} cm^{-1}) nm = 435 (5190); HRMS (ESI): Calcd for $C_{37}H_{50}N_4O_5Rh_2$ (M^+): 836.1891; Found: 836.1915. HRMS (ESI): Calcd for $C_{38}H_{52}N_4O_6Rh_2Na$ ([M + Na]$^+$): 889.1895; Found: 889.1490. $C_{38}H_{52}N_4O_6Rh_2$ (M^+): 866.1997; Found: 866.1887.

***trans*-{σ-(4-*N*,*N*-Dimethylaminophenyl)-σ-(3-formylphenyl)}-*tetrakis*-μ-(caprolactamato)dirhodium(III) (1n).** Orange solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.99 (s, 1H), 8.09 (s, 1H), 7.87 (d, J = 7.6 Hz, 1H), 7.62 (d, J = 7.6 Hz, 1H), 7.31 (d, J = 8.4 Hz, 2H), 7.27 (t, J = 7.6 Hz, 1H), 6.69 (d, J = 8.4 Hz, 2H), 3.07 (comp, 2H), 3.00–2.93 (comp, 12H), 2.48–2.34 (comp, 8H), 1.82 (comp, 2H), 1.68–1.35 (comp, 20H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.9, 184.1, 183.8, 149.0, 147.9 (d, J = 39.3 Hz), 143.9, 139.1, 136.2, 135.3, 130.7 (d, J = 37.8 Hz), 126.6, 125.8, 112.8, 51.7, 51.6, 41.5, 39.0, 38.9, 30.8, 29.9, 29.7, 24.5, 24.4; UV-visible (CH_2Cl_2): λ_{max} (ε M^{-1} cm^{-1}) = 430 (4090); IR (neat) 1689, 1585 cm^{-1}; HRMS (ESI): Calcd for $C_{39}H_{55}N_5O_5Rh_2Na$ ([M + Na]$^+$): 902.2211; Found: 902.1608.

***trans*-(σ-4-Trifluoromethylphenyl-σ-4-nitrophenyl)-*tetrakis*-μ-(caprolactamato)dirhodium(III) (1m).** Green solid; ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.95 (d, J = 8.8 Hz, 2H), 7.77 (d, J = 8.8 Hz, 2H), 7.65 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 2.97 (comp, 8H), 2.52–2.34 (comp, 8H), 1.80 (comp, 4H), 1.65–1.40 (comp, 20H); This compound was insoluble in all NMR solvents to the extent that its ^{13}C NMR spectrum was not obtained. UV-visible (CH_2Cl_2): λ_{max} (ε M^{-1} cm^{-1}) = 430 (8860); HRMS (ESI): Calcd for $C_{37}H_{48}N_5O_6Rh_2$ (M^+): 921.1667; Found: 921.1696.

Notes and references

1 J. M. Nichols, J. Wolf, Peter Zavalij, B. Varughese and M. P. Doyle, *J. Am. Chem. Soc.*, 2007, **129**, 3504.
2 J.-H. Xie, J. M. Nichols, C. Lubek and M. P. Doyle, *Chem. Commun.*, 2008, 2671.
3 J. Wolf, R. Poli, J.-H. Xie, J. Nichols, B. Xi, P. Zavalij and M. P. Doyle, *Organometallics*, 2008, **27**, 5836.
4 G.-L. Xu, R. J. Crutchley, M. C. DeRosa, Q.-J. Pan, H.-X. Zhang, X. Wang and T. Ren, *J. Am. Chem. Soc.*, 2005, **127**, 13354; A. S. Blum, T. Ren, D. A. Parish, S. A. Trammell, M. H. Moore, J. G. Kushmerick, G.-L. Xu, J. R. Deschamps, S. K. Pollack and R. J. Shashidhar, *J. Am. Chem. Soc.*, 2005, **127**, 10010; L. Chen, C. M. Ramsey, N. S. Dalal, T. Ren, F. A. Cotton, W. Wernsdorfer and I. Chiorescu, *Appl. Phys. Lett.*, 2006, **89**, 252502; J.-W. Ying, A. Cordova, G.-L. Xu and T. Ren, *Chem.–Eur. J.*, 2007, **13**, 6874.
5 J.-W. Ying and T. Ren, *J. Organomet. Chem.*, 2008, **693**, 1449; T. Ren, *Organometallics*, 2005, **24**, 4854.
6 K. M. Kadish, T. D. Phan, L. Giribabu, E. Van, Caemelbecke and J. L. Bear, *Inorg. Chem.*, 2003, **42**, 8663.
7 H. Nishiyama, J. Ito, T. Shiomi, T. Hashimoto, T. Miyakawa and M. Kitase, *Pure Appl. Chem.*, 2008, **80**, 743; Y. Motoyama, H. Narusawa and H. Nishiyama, *Chem. Commun.*, 1999, 131; Y. Motoyama, M. Okano, H. Narusawa, N. Makihara, K. Aoki and H. Nishiyama, *Organometallics*, 2001, **20**, 1580.
8 P. Zuman, *The Elucidation of Organic Electrode Processes*, Academic Press, New York, 1969.
9 C. Hansch, A. Leo and R. W. Taft, *Chem. Rev.*, 1991, **91**, 165.
10 T. Ren, Coord, *Chem. Rev.*, 1998, **175**, 43.
11 K. Costuas, F. Paul, L. Toupet, J.-F. Halet and C. Lapinte, *Organometallics*, 2004, **23**, 2053; F. Paul, J.-Y. Mevellec and C. Lapinte, *J. Chem. Soc., Dalton Trans.*, 2002, 1783.
12 H. T. Chifotides, and K. R. Dunbar, in *Multiple Bonds Between Metal Atoms*, 3rd Edition, ed. F. A. Cotton, C. A. Murillo, R. A. Walton, Springer Science, New York, 2005, Chapter 12.
13 T. Ren, in *Multiple Bonds Between Metal Atoms*, ed. F. A. Cotton, C. A. Murillo and R. A. Walton, Springer Science, New York, 3rd edn, 2005, ch. 10.
14 K. M. Kadish, R. Garcia, T. Phan, J. Wellhoff, E. Van, Caemelbecke and J. L. Bear, *Inorg. Chem.*, 2008, **47**, 11423; G. Zou;, J. C. Alverez and T. Ren, *J. Organomet. Chem.*, 2000, **596**, 152.
15 W.-Z. Chen, V. De, Silva, C. Lin, J. Abellard, D. M. Marcus and T. Ren, *J. Cluster Chem.*, 2005, **16**, 151; C. Lin, T. Ren, E. J. Valente and J. D. Zubkowski, *J. Organomet. Chem.*, 1999, **579**, 114.
16 M. P. Doyle, L. J. Westrum, W. N. E. Wolthuis, M. M. See, W. P. Boone, V. Bagheri and M. M. Pearson, *J. Am. Chem. Soc.*, 1993, **115**, 958.