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Rhodium and Iridium Complexes with the 1-(2-(Dimethylamino)ethyl)-2,3,4,5-tetramethylcyclopentadienyl Ligand

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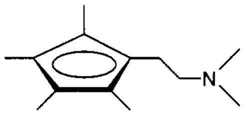
Some new Rh(I), Rh(III), Ir(I), and Ir(III) complexes containing the 1-(2-(dimethylamino)-ethyl)-2,3,4,5-tetramethylcyclopentadienyl (Cp^) ligand are described. The bis(ethene) complexes $Cp^\wedge Rh(C_2H_4)_2$ (**2**) and $Cp^\wedge Ir(C_2H_4)_2$ (**3**) with a noncoordinating dimethylamino function are synthesized by reaction of $[(C_2H_4)_2RhCl]_2$ with $Cp^\wedge Li$ and by reaction of $[(COE)_2IrCl]_2$ with $Cp^\wedge Li/C_2H_4$, respectively. Addition of iodine to **2** or **3** results in the formation of the respective diiodo complexes $Cp^\wedge RhI_2$ (**4**) and $Cp^\wedge IrI_2$ (**5**) with intramolecular amino coordination. In the presence of CO, **4** or **5** can easily be transferred into the carbonyl complexes $Cp^\wedge RhI_2(CO)$ (**6**) and $Cp^\wedge IrI_2(CO)$ (**7**), respectively, with a noncoordinating amino function. The reverse reaction is successful for both **6** and **7**, but under differing conditions. In the reaction of **4** and **5** with PMe_3, PPh_3, and CN^tBu, the corresponding substitution products $Cp^\wedge MI_2L$ (**8**−**12**) are formed. Reduction of **4** and **5** with sodium amalgam under a CO atmosphere leads to the carbonyl complexes $Cp^\wedge Rh(CO)_2$ (**13**) and $Cp^\wedge Ir(CO)_2$ (**14**), respectively, with a noncoordinating amino group. In the reaction of **4** and **5** with $Ag_2C_2O_4$, the oxalato complexes $Cp^\wedge RhC_2O_4$ (**15**) and $Cp^\wedge IrC_2O_4$ (**16**), respectively, are formed. The coordinating amino group in **15** and **16** can be replaced by the PMe_3 ligand (compounds $Cp^\wedge(PMe_3)RhC_2O_4$ (**17**) and $Cp^\wedge(PMe_3)IrC_2O_4$ (**18**)). Structure investigations on **4** (crystal system monoclinic; space group $P2_1/n$; $a = 8.775(5)$ Å; $b = 14.053(6)$ Å; $c = 13.880(7)$ Å; $\beta = 103.64(4)°$; $Z = 4$) and **5** (crystal system monoclinic; space group $P2_1/n$; $a = 8.828(2)$ Å, $b = 14.006(4)$ Å; $c = 13.823(4)$ Å; $\beta = 103.14(2)°$; $Z = 4$) confirm the intramolecular coordination of the dimethylamino group.

Introduction

Complexes with cyclopentadienyl ligands that bear a functionalized side chain may play an important role in catalytic processes. For example, immobilization of catalytically active complexes can proceed via reaction of the support with the cyclopentadienyl functionality.[1] Furthermore, enhanced water solubility may be achieved, for example, by quaternization of an amino group in the side chain.[2] Finally, the additional functionality can temporarily block a vacant coordination site at a metal center by reversible intramolecular coordination. According to this strategy it should be possible to stabilize reactive intermediates in catalytic reactions and to gain new information regarding the mechanism of catalytic processes.

Chart 1



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Very recently, we have introduced the polydentate 1-(2-(dimethylamino)ethyl)-2,3,4,5-tetramethylcyclopentadienyl ligand[3] (**1**) into the chemistry of s-, p-, d-, and f-block elements with some typical examples.[4] As a part of this work, we have investigated cobalt complexes with **1**.[5] We found the first example of intramolecular coordination of a polydentate cyclopentadienyl ligand at a cobalt(III) center. The intramolecularly coordinating dimethylamino group could be displaced irreversibly by phosphines and *tert*-butyl isocyanide and reversibly by carbon monoxide. This was the first time the reversible displacement of the additional functionality of a polydentate cyclopentadienyl ligand from a metal center was successful under mild conditions.

In an extension of our studies of complexes with **1** we now report the synthesis of rhodium and iridium compounds; here again, special emphasis is put on the coordination mode of the dimethylamino group.

Results

Treating a solution of $[(C_2H_4)_2RhCl]_2$ in THF with a solution of the lithiated ligand **1** ($Cp^\wedge Li$) yields the desired bis(ethene)rhodium complex **2** in very good yield. The analogous iridium complex **3** is obtained when $[(COE)_2IrCl]_2$[6] is treated with $Cp^\wedge Li$ under an atmosphere of ethene.

The ^1H NMR spectra[7] of **2** and **3** show that two molecules of ethene are coordinated to the metal centers.

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[1] Jutzi, P.; Heidemann, T.; Neumann, B.; Stammler, H.-G. *J. Organomet. Chem.* **1994,** *472,* 27−38.

[2] Avey, A.; Weakley, T. J. R.; Tyler, R. *J. Am. Chem. Soc.* **1993,** *115,* 7706−7715 and references cited therein.

[3] Jutzi, P.; Dahlhaus, J. *Synthesis* **1993,** 684−686.

[4] (a) Jutzi, P.; Dahlhaus, J.; Kristen, M. O. *J. Organomet. Chem.* **1993,** *450,* C1−C3. (b) Jutzi, P.; Dahlhaus, J.; Bangel, M. *J. Organomet. Chem.* **1993,** *460,* C13−C15.

[5] Jutzi, P.; Kristen, M. O.; Dahlhaus, J.; Neumann, B.; Stammler, H.-G. *Organometallics* **1993,** *12,* 2980−2985.

[6] COE: cyclooctene (C_8H_{14}).

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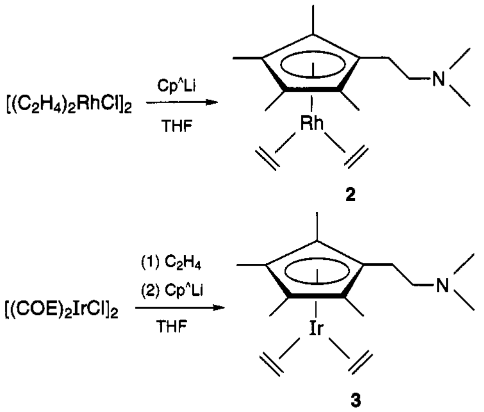
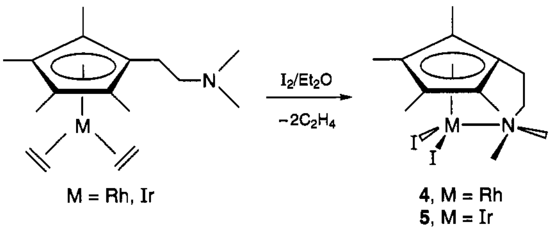
Scheme 1



Scheme 2



For **2** two broad featureless signals centered at 1.22 and 1.74 ppm are observed for the ethene hydrogen atoms at room temperature; they become well resolved but complex at −20 °C in CD_2Cl_2 solution (centers of the multiplets 1.16 and 1.72 ppm). The ethene units in **3** exhibit two well-resolved but complicated multiplets centered at 0.73 and 1.50 ppm. These multiplicity patterns (AA′BB′ spin system) are similar to those for known ethene compounds of cyclopentadienyl complexes with rhodium and iridium.[8] In addition, for both molecules all other ^1H and ^{13}C NMR data are in agreement with the noncoordination of the dimethylamino group, as they are very similar to data recorded for a molybdenum dicarbonyl complex of **1** where the noncoordination of the side chain has been proved by an X-ray crystal structure analysis.[4a,9]

Addition of iodine to an ethereal solution of **2** or **3** results in loss of the two ethene molecules and formation of the oxidative-addition products **4** and **5**, respectively, in which the side chain coordinates in an intramolecular manner. The ^1H and ^{13}C NMR data for these complexes show some remarkable differences compared with the data of **2** and **3**. The most significant change in the ^1H NMR spectra is caused by the low-field shift for the signals of the methylene hydrogen atoms adjacent to the nitrogen atom of the side chain. While for the complexes **2** and **3** these signals are observed at about 2.3 ppm, **4** and **5** show values of 3.48 and 3.62 ppm, respectively. In addition, the signals for the methyl groups at the nitrogen atoms are shifted downfield (0.6 and 0.8 ppm, respectively). Corresponding downfield shifts for the methylene and methyl groups adjacent to the nitrogen atom are observed in the ^{13}C NMR spectra. The signals for both groups are shifted 11−17 ppm downfield for the complexes **4** and **5** compared with **2** and **3**, respectively. These NMR data strongly suggest that the dimethylamino group is coordinated intramolecularly to the metal center. The coordination to the metal causes a deshielding of the relevant atoms and results in a downfield shift. Additional evidence for the intramolecular coordination of the dimethylamino group in **4** and **5** arises from the change of the multiplicity pattern for the signals of the methylene hydrogen atoms. In **2** and **3** they appear as multiplets; here they show clean triplets. A very fast flip of the side chain that is coordinated to the metal center in a zigzag fashion (*vide infra*) causes averaged signals for both methylene groups; therefore, triplets are found for these hydrogen atoms. No substantial broadening of these signals is observed even at −70 °C, indicating that the fluxional process is fast on the ^1H NMR time scale. In the case of the rhodium complex **4** there is another valuable ^1H NMR probe for an intramolecular coordination. In addition to the downfield shift for the signal of the methyl groups adjacent to the nitrogen atom, this signal is split into a doublet with a coupling constant of 1.1 Hz. This coupling is caused by the interaction of the hydrogen atoms with the ^{103}Rh nucleus. Final proof for the intramolecular coordination in **4** and **5** is provided by X-ray crystal structure analyses. Suitable crystals are obtained by slow diffusion of *n*-hexane into dichloromethane solutions of **4** and **5**, respectively. Both solid-state structures consist of monomeric molecules where the dimethylamino group is intramolecularly coordinated to the central atom (see Figures 1 and 2 and Tables 1−5). The metal−nitrogen distances are 2.241(5) and 2.218(10) Å, respectively. These distances are only slightly longer than the Co−N bond in the corresponding cobalt complex.[5] The lengths of the M−I bonds are 2.7238(11) and 2.712(2) Å for M = Rh and 2.7182(11) and 2.7075(12) Å for M = Ir. The distances between the respective metals and the ring carbons vary in the range of 2.097(6)−2.194(7) Å (M = Rh) and 2.109(12)−2.201(12) Å (M = Ir). Thus, the metal atoms are not exactly centered below the cyclopentadienyl ring but shifted to C(1) by a small extent. In addition, the structures show that the methylene carbon atom of the side chain (C(10)) is bent by 9.6 and 10.7° toward the metal, respectively. Another noteworthy detail is that the side chain is coordinated to the relevant metal in a

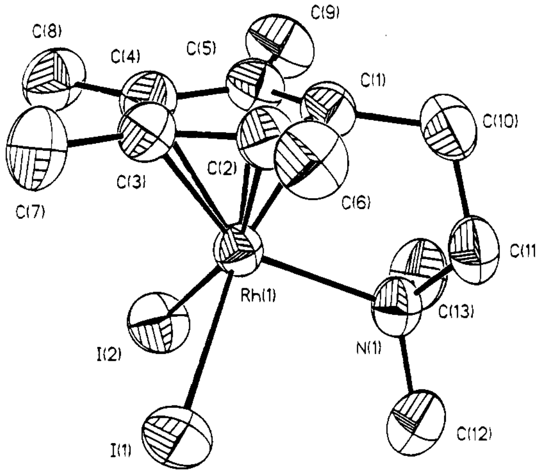


Figure 1. Plot of the molecular structure of **4**, with thermal ellipsoids at the 50% probability level.

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(7) The ^1H NMR spectra are subject to rather large solvent shifts. Comparisons were made from spectra recorded in $CDCl_3$.

(8) (a) Cramer, R.; Mrowca, J. J. *Inorg. Chim. Acta* **1971**, *5*, 528−530. (b) Moseley, K.; Kang, J. W.; Maitlis, P. W. *J. Chem. Soc. A* **1970**, 2875−2883.

(9) Kristen, M. O. Diploma Thesis, Universität Bielefeld, 1992.

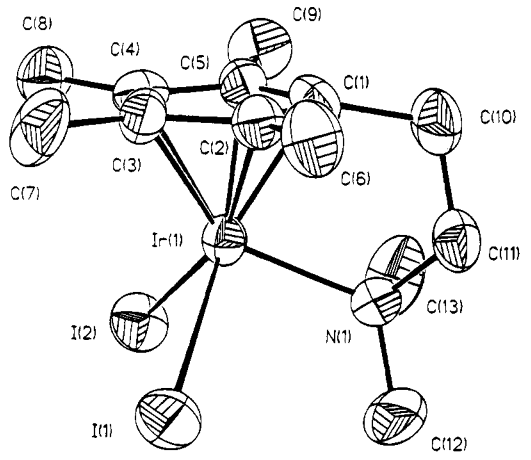


Figure 2. Plot of the molecular structure of **5**, with thermal ellipsoids at the 50% probability level.

Table 1. Crystallographic Data for Diffraction Studies of 4 and 5

empirical formula	$C_{13}H_{22}I_2NRh$	$C_{13}H_{22}I_2IrN$
cryst size, mm³	0.60 × 0.50 × 0.30	0.50 × 0.30 × 0.10
fw	549.03	638.32
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
lattice params		
a, Å	8.775(5)	8.828(2)
b, Å	14.053(6)	14.006(4)
c, Å	13.880(7)	13.823(4)
α, deg	90	90
β, deg	103.64(4)	103.14(2)
γ, deg	90	90
V, Å³	1663(2)	1664.4(8)
Z	4	4
d_{calc} g/cm³	2.19	2.547
diffractometer	Siemens $P2_1$	Siemens $P2_1$
F(000)	1032	1160
μ(Mo Kα), mm⁻¹	4.721	11.714
temp, °C	20(2)	20(2)
$2\theta_{max}$, deg	60	60
no. of data collected	5128	5180
no. of obsd data ($F > 4\sigma(F)$)	3722	2917
no. of params refined	161	161
residuals: *R*1	0.0527	0.0567
largest peak in final diff map, e/Å³	1.3	2.2
abs cor	semiempirical	semiempirical

zigzag fashion. All the described structural features are similar to those of the corresponding cobalt complex.[5]

The reversible displacement of the intramolecularly coordinating dimethylamino group by carbon monoxide is successful for both **4** and **5**, but under differing conditions. Bubbling carbon monoxide through a $CDCl_3$ solution of **4** leads to complete conversion into the carbonyl complex **6**. Both ^1H and ^{13}C NMR data for **6** are consistent with the noncoordination of the side chain, as they are very similar to the data for **2**. The presence of the carbonyl ligand is proved by ^{13}C NMR (δ 180.9 ppm (d), $J_{Rh-C} = 69$ Hz) and IR (ν 2060 cm^{-1}) spectroscopy. As indicated by the absorption at high wavenumber, the carbon monoxide is only very weakly bound to the rhodium center. Therefore, **6** is only stable under an atmosphere of carbon monoxide. Attempts to remove this atmosphere either by applying vacuum or simply by bubbling argon through the solution result immediately in the complete loss of the CO ligand and in the formation of **4**. This reversible reaction can be repeated several times without the observation of any other products.

Table 2. Atomic Coordinates (×10⁴) and Isotropic Displacement Parameters *U*(eq)[a] (Å² × 10³) for 4

	x	*y*	*z*	*U*(eq)
Rh(1)	1591(1)	2404(1)	4668(1)	43(1)
I(1)	1301(1)	1122(1)	3164(1)	65(1)
I(2)	−1486(1)	2890(1)	4175(1)	69(1)
N(1)	2285(7)	3633(4)	3836(4)	53(1)
C(1)	3622(7)	2822(4)	5710(5)	50(1)
C(2)	3778(7)	1838(4)	5510(5)	50(1)
C(3)	2520(8)	1336(4)	5806(5)	51(1)
C(4)	1627(8)	2011(5)	6204(5)	53(1)
C(5)	2295(8)	2937(5)	6167(5)	51(1)
C(6)	5076(9)	1368(6)	5161(6)	64(2)
C(7)	2309(11)	277(5)	5785(7)	72(2)
C(8)	292(9)	1779(6)	6654(6)	68(2)
C(9)	1806(10)	3809(6)	6617(7)	72(2)
C(10)	4497(9)	3603(5)	5344(6)	63(2)
C(11)	4025(9)	3635(5)	4202(6)	62(2)
C(12)	1899(1)	3549(7)	2736(6)	74(2)
C(13)	1654(11)	4555(5)	4090(7)	73(2)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Atomic Coordinates (×10⁴) and Isotropic Displacement Parameters *U*(eq)[a] (Å² × 10³) for 5

	x	*y*	*z*	*U*(eq)
Ir(1)	1569(1)	7408(1)	4640(1)	38(1)
I(1)	1241(1)	6140(1)	3119(1)	60(1)
I(2)	−1478(1)	7895(1)	4149(1)	64(1)
N(1)	2237(12)	8612(7)	3780(7)	46(2)
C(1)	3596(14)	7824(8)	5685(9)	44(3)
C(2)	3730(13)	6848(9)	5474(9)	43(3)
C(3)	2528(14)	6338(8)	5782(9)	43(3)
C(4)	1641(15)	7018(9)	6169(9)	46(3)
C(5)	2292(15)	7958(9)	6120(9)	45(3)
C(6)	5043(16)	6389(10)	5089(11)	59(3)
C(7)	2307(21)	5272(9)	5753(11)	71(5)
C(8)	290(16)	6778(11)	6638(10)	61(4)
C(9)	1772(19)	8815(10)	6612(11)	68(4)
C(10)	4475(17)	8627(9)	5276(11)	59(4)
C(11)	3967(15)	8627(9)	4150(10)	53(3)
C(12)	1853(22)	8524(11)	2670(10)	80(5)
C(13)	1611(22)	9565(10)	4034(14)	84(5)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 4

Rh(1)—C(1)	2.097(6)	Rh(1)—C(1)	2.150(6)
Rh(1)—C(5)	2.159(6)	Rh(1)—C(3)	2.191(6)
Rh(1)—C(4)	2.194(7)	Rh(1)—N(1)	2.241(5)
Rh(1)—I(2)	2.712(2)	Rh(1)—I(1)	2.7238(11)
N(1)—C(12)	1.488(10)	N(1)—C(13)	1.485(9)
N(1)—C(11)	1.491(9)	C(1)—C(2)	1.423(8)
C(1)—C(5)	1.460(9)	C(1)—C(10)	1.496(9)
C(2)—C(3)	1.449(9)	C(2)—C(6)	1.493(9)
C(3)—C(4)	1.422(9)	C(3)—C(7)	1.500(9)
C(4)—C(5)	1.433(9)	C(4)—C(8)	1.488(9)
C(5)—C(9)	1.485(9)	C(10)—C(11)	1.542(11)
C(1)—Rh(1)—N(1)	81.4(2)	C(3)—C(4)—C(5)	108.9(5)
N(1)—Rh(1)—I(2)	92.9(2)	C(4)—C(5)—C(1)	106.9(5)
N(1)—Rh(1)—I(1)	95.9(2)	C(1)—C(10)—C(11)	109.6(6)
C(12)—N(1)—C(13)	107.8(6)	I(2)—Rh(1)—I(1)	93.77(4)
C(13)—N(1)—C(11)	109.1(6)	C(12)—N(1)—C(11)	108.4(6)
C(13)—N(1)—Rh(1)	112.8(4)	C(12)—N(1)—Rh(1)	116.4(4)
C(2)—C(1)—C(5)	108.4(5)	C(11)—N(1)—Rh(1)	101.9(4)
C(1)—C(2)—C(3)	107.6(5)	C(10)—C(1)—Rh(1)	113.1(5)
C(4)—C(3)—C(2)	108.2(5)	N(1)—C(11)—C(10)	110.8(6)
C(2)—C(3)—Rh(1)	69.0(3)		

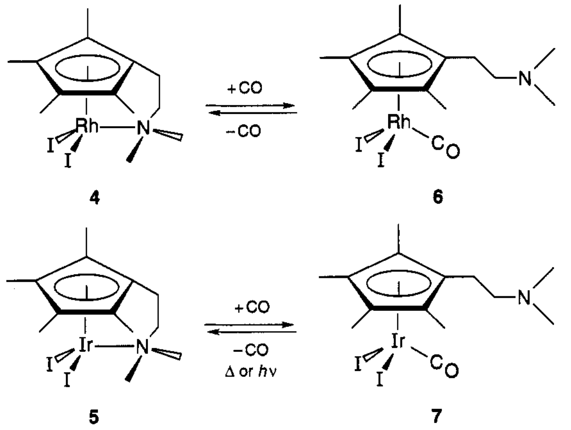
In contrast to the very labile rhodium carbonyl compound **6**, the analogous iridium complex **7** is stable enough to be isolated in excellent yield. Compound **7** is prepared by stirring a dichloromethane solution of **5** under an atmosphere of carbon monoxide. All spectroscopic data for **7** are consistent with the proposed

Table 5. Selected Bond Lengths (Å) and Angles (deg) for 5

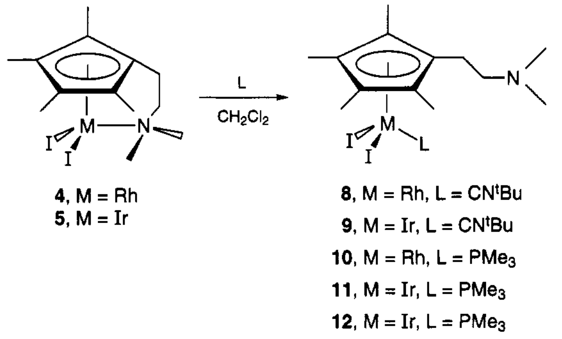
Ir(1)—C(1)	2.109(12)	Ir(1)—C(2)	2.141(12)
Ir(1)—C(5)	2.142(12)	Ir(1)—C(4)	2.169(12)
Ir(1)§bc(3)	2.201(12)	Ir(1)—N(1)	2.218(10)
Ir(1)—I(2)	2.7075(12)	Ir(1)—I(1)	2.7182(11)
N(1)—C(11)	1.50(2)	N(1)—C(12)	1.50(2)
N(1)—C(13)	1.52(2)	C(1)—C(2)	1.41(2)
C(1)—C(5)	1.43(2)	C(1)—C(10)	1.55(2)
C(2)—C(3)	1.42(2)	C(2)—C(6)	1.52(2)
C(3)—C(4)	1.41(2)	C(3)—C(7)	1.50(2)
C(4)—C(5)	1.44(2)	C(4)—C(8)	1.52(2)
C(5)—C(9)	1.50(2)	C(10)—C(11)	1.52(2)

C(1)—Ir(1)—N(1)	82.5(4)	C(3)—C(4)—C(5)	109.6(10)
N(1)—Ir(1)—I(2)	92.5(3)	C(1)—C(5)—C(4)	105.5(10)
N(1)—Ir(1)—I(1)	94.4(3)	C(11)—C(10)—C(1)	108.6(11)
C(11)—N(1)—C(12)	109.0(11)	I(2)—Ir(1)—I(1)	92.6(4)
C(12)—N(1)—C(13)	107.5(12)	C(11)—N(1)—C(13)	107.8(11)
C(12)—N(1)—Ir(1)	117.4(8)	C(11)—N(1)—Ir(1)	101.7(7)
C(2)—C(1)—C(5)	109.2(10)	C(13)—N(1)—Ir(1)	112.9(8)
C(1)—C(2)—C(3)	108.7(10)	C(10)—C(1)—Ir(1)	111.6(9)
C(4)—C(3)—C(2)	106.9(11)	C(9)—C(5)—Ir(1)	131.6(10)
C(2)—C(3)—Ir(1)	68.6(7)	N(1)—C(11)—C(10)	113.0(11)

Scheme 3



Scheme 4



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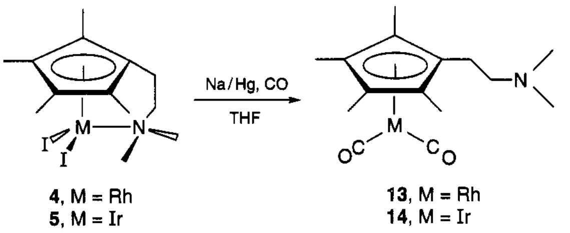
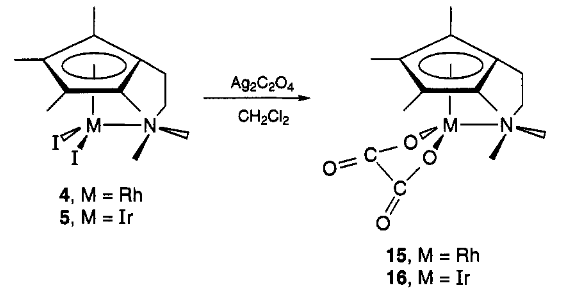


Scheme 6



structure. Surprisingly, removal of the carbonyl ligand turns out to be difficult. After a C_6D_6 solution of **7** is irradiated for 2 h, an almost 50% conversion back to **5** and further formation of a yet unknown compound is observed; no starting material can be detected. A cleaner reaction takes place when a toluene solution of **7** is heated to reflux for 4 h. Here the ^{1}H NMR spectrum only shows signals for the desired complex **5** and unreacted starting material **7** in a 1:5 ratio. No reaction is observed when **4** or **5** is treated with ethene.

Treatment of the rhodium complex **4** with *tert*-butyl isocyanide or trimethylphosphine in dichloromethane solution yields the complexes **8** and **10**, respectively. Similarly, the iridium compounds **9**, **11**, and **12** are obtained by reaction of a dichloromethane solution of **5** with *tert*-butyl isocyanide, trimethylphosphine, and triphenylphosphine, respectively. All these complexes with an uncoordinated dimethylamino group could not be obtained in analytically pure form but are characterized by NMR spectroscopy and mass spectrometry. The spectroscopic data for the complexes **8**−**12** prove that the dimethylamino group of the side chain is decomplexed from the metal center in all cases. They further show that only one additional ligand is bound to the metal. The *tert*-butyl isocyanide complexes **8** and **9** exhibit the expected IR absorption for the isocyanide unit at 2185 and 2173 cm^{-1}, respectively. For the phosphine complexes **10**−**12** the resonances in the ^{31}P NMR spectra are in the expected range; the signal for the rhodium trimethylphosphine complex **8** is split into a doublet (J_{Rh-P} = 135 Hz) by coupling to the rhodium center.

When **4** and **5** are reduced with sodium amalgam under an atmosphere of carbon monoxide, the dicarbonyl complexes **13** and **14** are respectively obtained in good yields. The ^{1}H and ^{13}C NMR data for these compounds are similar to those for the corresponding ethene complexes **2** and **3**; therefore, a noncoordination of the side chain can be assumed. Additional evidence for the proposed structures is provided by the IR spectra. Both spectra show two absorptions (**13**, 1987, 1940 cm^{-1}; **14**, 2018, 1936 cm^{-1}) in the region where similar rhodium and iridium cyclopentadienyl dicarbonyl complexes absorb.[10] The rhodium complex **13** seems to be quite unstable, as it changes its color rather rapidly from yellow-brown to blue after isolation; therefore, no satisfactory microanalysis could be obtained. The nature of the blue product has not been determined yet.

Treatment of dichloromethane solutions of **4** and **5** with silver oxalate for several days under the exclusion of light yields the desired complexes **15** and **16**, respectively, where the side chain still coordinates intramolecularly.

The coordination behavior of the dimethylamino group is discussed by comparison of the ^{1}H and ^{13}C NMR data for **15** and **16** with the data for **4** and **5**. Both oxalato complexes show triplets for the methylene

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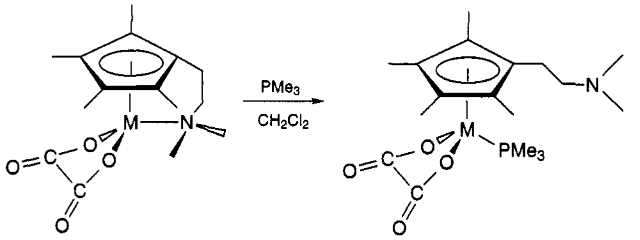
(10) Kang, J. W.; Maitlis, P. M. *J. Organomet. Chem.* **1971**, *26*, 393−399.

Scheme 7



15, M = Rh
16, M = Ir

17, M = Rh
18, M = Ir

groups adjacent to the nitrogen atom at 3.66 and 3.77 ppm, respectively, in the ^1H NMR spectra, typical for complexes where the side chain of **1** is coordinated intramolecularly to the metal (see above).[4a,5] For the rhodium complex **15** the assumption of intramolecular coordination is further supported by coupling of the hydrogen atoms of the dimethylamino group with the rhodium center (J_{Rh-H} = 0.8 Hz). The ^{13}C NMR data show the expected downfield shifts for the methyl and methylene carbon atoms attached to the nitrogen atom compared with complexes with a noncoordinated side chain. The signals for the carbonyl atoms of the oxalate group of **15** and **16** appear in the expected region at 166.0 and 165.7 ppm in the ^{13}C NMR spectra, respectively. In the IR spectra the absorptions of the C=O units are detected at 1678 and 1650 cm^{-1}, respectively.

The displacement of the dimethylamino group in **15** and **16** with carbon monoxide under normal pressure is not successful. When CO is bubbled through $CDCl_3$ solutions of **15** and **16**, no changes can be detected in the ^1H NMR spectra recorded immediately after the exposure to CO. In contrast, treatment of **15** and **16** with trimethylphosphine leads to decomplexation of the side chain and formation of **17** and **18**, respectively. In the ^1H NMR spectra both complexes show doublets for the methyl groups at the cyclopentadienyl ring, caused by coupling with the coordinated trimethylphosphine. The signal in the ^{31}P NMR spectrum for the trimethylphosphine in **17** is split into a doublet (J = 156 Hz) by $^{31}P-^{103}Rh$ coupling.

Discussion

With easily accessible precursors as starting materials, the synthesis of a variety of rhodium and iridium complexes with the 1-(2-(dimethylamino)ethyl)-2,3,4,5-tetramethylcyclopentadienyl ligand was successful. For the ethene complexes **2** and **3** with a metal center in the formal oxidation state I an intramolecular coordination of the dimethylamino group could not be observed. It is favorable for an electron-rich metal to donate electron density to a π-electron acceptor (here ethene) rather than to increase its electron density by coordination of a donor ligand (here the dimethylamino group in the side chain). Therefore, the bis(ethene) complexes are formed in favor of the mono(ethene) complexes with an intramolecularly coordinated dimethylamino group.

Oxidation of the bis(ethene) complexes **2** and **3** with iodine yields **4** and **5**, respectively, where the side chain coordinates intramolecularly to the metal center. It is very likely that these reactions proceed via the Cp^MI$_2$-(C_2H_4) intermediates. Due to the oxidation process the metal centers now favor coordination of a strong donor rather than an acceptor ligand that is only a weak electron donor. Therefore, the ethene ligand of the intermediates is immediately substituted by the dimethylamino group of the side chain. The corresponding pentamethylcyclopentadienyl complexes of **4** and **5** ($[C_5Me_5MI_2]_2$, M = Rh, Ir)[11] do not have the possibility of stabilizing themselves in the described manner; therefore, the vacant coordination site is occupied by dimerization.

The coordination mode of the dimethylamino group in **4** and **5** is proved by X-ray crystal structure analysis. To our knowledge there has been only one other report of an iridium complex with a functionalized cyclopentadienyl ligand where the additional functionality coordinates intramolecularly,[12] but no structural data are available. The rhodium complex **4** is the first of its kind.

The irreversible displacement of the dimethylamino group from the metal in **4** and **5** is successful with more strongly donating ligands such as phosphines and *tert*-butyl isocyanide.[13] While the complexes **4** and **5** failed to react with ethene to yield complexes of the type Cp^-MI$_2$(C_2H_4) (for reasons described above), the side chain can easily be displaced reversibly by carbon monoxide to give complexes **6** and **7**, respectively. The donating abilities of CO are strong enough to compete with the dimethylamino group coordination at the metal(III) center, although the intramolecular coordination is entropically favored. In the case of the rhodium complex **6** the reaction is completely reversible under very mild conditions, whereas for the iridium compound **7** rather drastic conditions are required to eliminate CO. Loss of CO is observed in refluxing toluene, at least partially. It is expected that prolonged heating of **7** will result in quantitative loss of carbon monoxide and formation of **5**.

Reduction of **4** and **5** with sodium amalgam yields the dicarbonyl complexes **13** and **14**, respectively, with a noncoordinated side chain rather than the corresponding monocarbonyl complexes Cp^M(CO) with additional coordination of the dimethylamino group. The explanation for this result is analogous to that described for the bis(ethene) complexes.

Interestingly, the iodine atoms in the complexes **4** and **5** can be cleanly substituted by oxalate with retention of the intramolecularly coordinated dimethylamino group. Unfortunately, no crystals suitable for X-ray diffraction studies could be obtained for **15** and **16**, respectively.[14] The coordination mode of the side chain is determined by careful comparison of the NMR data with the data for **4** and **5**.

In **15** and **16**, the dimethylamino group was displaced successfully by the strong donor trimethylphosphine but not by carbon monoxide. Presumably the oxalate group in **15** and **16** is more electron withdrawing than the two

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[11] Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970–5977.

[12] Miguel-Garcia, J. A.; Adams, H.; Bailey, N. A.; Maitlis, P. W. *J. Organomet. Chem.* **1991**, *413*, 427–444.

[13] There is evidence that the dimethylamino group in **5** can be displaced even by DMSO. The ^{13}C NMR spectrum of **5** in DMSO-d_6 shows values that are nearly identical with those for the bis(ethene) complex **3** (with a noncoordinated dimethylamino group) in DMSO-d_6, whereas the spectrum in $CDCl_3$ shows remarkable differences.

[14] Very recently we were able to obtain a crystal structure of **15**, which is in full agreement with our predictions based on NMR data. Details will be published elsewhere.

iodine ligands in **4** and **5**. As a result the donor ability of CO is insufficient to substitute the dimethylamino group.

Conclusion

The results described in this paper show that the coordination mode of the 1-(2-(dimethylamino)ethyl)-2,3,4,5-tetramethylcyclopentadienyl ligand depends on the oxidation state of the corresponding metal center. Intramolecular coordination of the dimethylamino group could be achieved in rhodium(III) and iridium(III) complexes. For rhodium(I) and iridium(I) compounds the coordination of an acceptor ligand (such as ethene or carbon monoxide) is favored over intramolecular coordination of the side chain. The most interesting result, however, is that the dimethylamino group can be displaced reversibly in **4** and **5**. Here the side arm acts in the desired way as an intramolecular protection group of a vacant coordination site. We will continue to examine these systems with respect to their potential use in catalytic reactions.

Experimental Section

All experiments were carried out under an atmosphere of dry argon. When carbon monoxide or ethene was used as a reagent, the gas provided a protective atmosphere. Solvents were dried by using standard procedures and distilled prior to use. All other reagents were used as purchased. The irradiation experiment was performed using a Hanau TQ 150 high-pressure mercury lamp. All NMR spectra were obtained using a Bruker AM 300 spectrometer on solutions in $CDCl_3$, C_6D_6, or DMSO-d_6 as noted. The spectra were calibrated using signals of residual protons from the solvents referenced to $SiMe_4$. Shifts quoted for the ^{31}P NMR spectra are relative to 85% H_3PO_4. The mass spectra were determined by using a VG AutoSpec. Only characteristic fragments and isotopes of the highest abundance are listed. Melting points were determined in sealed capillaries with a Büchi 510 melting point determination apparatus and are uncorrected. IR spectra were recorded on CH_2Cl_2 solutions on a Perkin-Elmer 598 infrared spectrophotometer. Only characteristic frequencies are listed. The CHN analyses were performed by Analytisches Labor der Fakultät für Chemie der Universität Bielefeld.

(2-(Dimethylamino)ethyl)tetramethylcyclopentadiene (Cp^H)[3], $[(C_2H_4)_2RhCl]_2$,[15] and $[(COE)_2IrCl]_2$[16] were prepared as described in the literature.

[η^5-1-(2-(Dimethylamino)ethyl)-2,3,4,5-tetramethylcyclopentadienyl]bis(η^2-ethene)rhodium(I) (2). A 4.54-g (11.7-mmol) amount of $[(C_2H_4)_2RhCl]_2$ was dissolved in 75 mL of THF. The reaction mixture was cooled to −60 °C. To this solution was added dropwise a THF solution of Cp^Li (prepared by addition of 15.0 mL (23.3 mmol) of *n*-butyllithium (1.6 M in *n*-hexane) to a solution of 4.50 g (23.3 mmol) of Cp^H in 80 mL of THF at −60 °C). The reaction mixture was warmed to room temperature within 1 h and then stirred for an additional 1 h. After the solvent of the resulting yellow-brown solution was removed in vacuo, the oily brown residue was extracted with 100 mL of *n*-hexane. The solution was filtered and the residue washed with 3 × 20 mL of *n*-hexane. The combined *n*-hexane extracts were evaporated in vacuo, leaving 7.33 g (20.9 mmol, 90%) of **2** as a brown air-stable oil. ^1H NMR ($CDCl_3$): δ 1.20−1.24 (m, 4H, inner 2*H* of C_2H_4), 1.65, 1.76 (2s, 2 × 6H, CH_3), 1.73−1.76 (m, 4H, outer 2*H* of C_2H_4), 2.21−2.38 (m, 2 × 2H, CH_2 and CH_2−N), 2.28 (s, 6H, N−CH_3). ^1H NMR (C_6D_6): δ 1.49−1.54 (m, 4H, inner 2*H* of C_2H_4), 1.56, 1.61 (s, 2 × 6H, CH_3), 1.95−2.03 (m, 4H, outer 2*H* of C_2H_4), 2.11 (s, 6H, N−CH_3), 2.23−2.28 (m, 2H, CH_2), 2.38−2.43 (m, 2H, CH_2−N). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 8.8, 9.4 (CH_3, 23.1 (CH_2), 43.7 (d, J_{Rh-C} = 14 Hz, C_2H_4), 45.4 (N−CH_3), 60.9 (CH_2−N), 96.1, 97.5, 98.9 (ring *C*). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 8.4 (d, J_{Rh-C} = 42 Hz, CH_3), 8.7 (d, J_{Rh-C} = 43 Hz, CH_3), 21.9 (d, J_{Rh-C} = 46 Hz, CH_2), 43.3 (d, J_{Rh-C} = 13 Hz, C_2H_4), 45.0 (N−CH_3), 60.2 (CH_2−N), 95.6, 96.9, 98.9 (ring *C*). MS (EI; *m/z* (relative intensity, %)): 293 ($[M - Me_2NCH_2]^+$, 79), 58 ($Me_2NCH_2^+$, 100). Anal. Calcd for $C_{17}H_{30}NRh$ (351.34): C, 58.12; H, 8.61; N, 3.99. Found: C, 56.74; H, 8.20; N, 3.82.

[η^5-1-(2-Dimethylamino)ethyl)-2,3,4,5-tetramethylcyclopentadienyl]bis(η^2-ethene)iridium(I) (3). A 5.10-g (5.70-mmol) amount of $[(COE)_2IrCl]_2$ was suspended in 200 mL of ether under an atmosphere of ethene. The yellow suspension turned into a red solution. The reaction mixture was stirred for 15 min at room temperature and then cooled to −70 °C. To this solution was added dropwise a THF solution of Cp^Li (prepared by addition of 7.4 mL (11.4 mmol) of *n*-butyllithium (1.6 M in *n*-hexane) to a solution of 2.20 g (11.4 mmol) of Cp^H in 40 mL of THF at −40 °C). The reaction mixture was warmed to room temperature within 1 h and then stirred for an additional 1 h. After the solvent of the resulting yellow-brown solution was removed in vacuo, the oily brown residue was extracted with 100 mL of *n*-hexane. The solution was filtered and the residue washed with 3 × 20 mL of *n*-hexane. The combined *n*-hexane extracts were evaporated in vacuo, leaving 3.95 g (8.97 mmol, 79%) of **3** as a brown air-stable oil. ^1H NMR ($CDCl_3$): δ 0.72−0.75 (m, 4H, inner 2*H* of C_2H_4), 1.49−1.52 (m, 4H, outer 2*H* of C_2H_4), 1.77, 1.79 (2s, 2 × 6H, CH_3), 2.22−2.33 (m, 2 × 2H, CH_2 and CH_2−N), 2.25 (s, 6H, N−CH_3). ^1H NMR (C_6D_6): δ 1.13−1.16 (m, 4H, inner 2*H* of C_2H_4), 1.59 (s, 2 × 6H, CH_3), 1.81−1.83 (m, 4H, outer 2*H* of C_2H_4), 2.09 (s, 6H, N−CH_3), 2.18−2.24 (m, 2H, CH_2), 2.31−2.36 (m, 2H, CH_2−N). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 8.4, 9.0 (CH_3), 23.4 (CH_2), 24.9 (C_2H_4), 45.6 (N−CH_3), 61.2 (CH_2−N), 92.1, 93.5, 94.9 (rings *C*). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 7.9, 8.5 (CH_3), 21.9 (CH_2), 23.6 (C_2H_4), 44.9 (N−CH_3), 59.9 (CH_2−N), 91.6, 93.0, 94.1 (ring *C*). MS (EI; *m/z* (relative intensity, %)): 441 (M^+, 12), 413 ($[M - C_2H_4]^+$, 39), 383 ($[M - Me_2NCH_2]^+$, 79), 58 ($Me_2NCH_2^+$, 100). High resolution MS (EI; *m/z*): calcd (^{193}Ir), 441.2008; found 441.1990. Anal. Calcd for $C_{17}H_{30}IrN$(440.65): C, 46.33; H 6.86; 3.18. Found: C, 46.36; H, 6.76; N, 3.18.

Diiodo[η^5:η^1-1-(2-(dimethylamino)ethyl)-2,3,4,5-tetramethylcyclopentadienyl]rhodium(III) (4). A solution of 0.26 g (1.02 mmol) of iodine in 10 mL of ether was added to a solution of 0.37 g (1.05 mmol) of **2** in 20 mL of ether. The immediate formation of a reddish precipitate was observed. After the reaction mixture has been stirred for 1 h, the solution decanted and the residue washed with 2 × 5 mL of ether. The residue was dried in vacuo, leaving 0.55 g (1.00 mmol, 98%) of **4** as a reddish solid. ^1H NMR ($CDCl_3$): δ 1.95, 2.13 (2s, 2 × 6H, CH_3), 2.20 (t, J = 6.4 Hz, 2H, CH_2), 2.81 (d, J_{Rh-H} = 1.1 Hz, 6H, N−CH_3), 3.48 (t, J = 6.4 Hz, 2H, CH_2−N). ^1H NMR (C_6D_6): δ 1.32 (t, J = 6.4 Hz, 2H, CH_2), 1.54, 1.58 (2s, 2 × 6H, CH_3), 2.41 (d, J_{Rh-H} = 0.9 Hz, 6H, N−CH_3), 2.50 (t, J = 6.4 Hz, 2H, CH_2−N). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 10.0, 12.6 (CH_3), 22.6 (CH_2), 56.8 (N−CH_3), 74.3 (CH_2−N), 89.9 (d, J_{Rh-C} = 8 Hz, ring *C*), 96.3 (d, J_{Rh-C} = 8 Hz, ring *C*), 106.4 (d, J_{Rh-C} = 8 Hz, ring *C*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 9.6, 12.4 (CH_3), 21.9 (CH_2), 56.4 (N−CH_3), 73.5 (CH_2−N), 98.9 (ring *C*). MS (EI; *m/z* (relative intensity,%)): 549 (M^+, 1), 422 ($[M - I]^+$, 11), 58 ($Me_2NCH_2^+$, 100). Mp: 188 °C dec. Anal. Calcd for $C_{13}H_{22}I_2NRh$(594.04): C, 28.42; H, 4.04; N, 2.55; I, 46.2. Found: C, 27.83; H, 4.22; N, 2.33; I, 45.1.

Diiodo[η^5:η^1-1-(2-(dimethylamino)ethyl)-2,3,4,5-tetramethylcyclopentadienyl]iridium(III) (5). A solution of 1.05 g (4.14 mmol) of iodine in 15 mL of ether was added to a solution of 1.89 g (4.30 mmol) of **3** in 30 mL of ether. The immediate formation of a tan-brown precipitate was observed. After the reaction mixture was stirred for 1 h, the solution

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(16) Herdé, J. L.; Senoff, C. V. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 1029−1031.

was decanted and the residue washed with 2 × 10 mL of ether. The residue was dried in vacuo, leaving 2.60 g (4.08 mmol, 98%) of **5** as a brown powder. ^{1}H NMR ($CDCl_3$): δ 1.81, 1.98 (2s, 2 × 6H, CH_3), 2.14 (t, J = 6.3 Hz, 2H, CH_2), 3.02 (s, 6H, N$-CH_3$), 3.62 (t, J = 6.3 Hz, 2H, CH_2-N). ^{1}H NMR (C_6D_6): δ 0.91 (t, J = 6.4 Hz, 2H, CH_2), 1.45, 1.50 (2s, 2 × 6H, CH_3), 2.59 (s, 6H, N$-CH_3$), 2.61 (t, J = 6.4 Hz, 2H, CH_2-N). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 9.3, 12.1 (CH_3), 22.7 (CH_2), 57.4 (N$-CH_3$), 79.4 (CH_2-N), 80.6, 88.5, 98.3 (ring *C*). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 9.9, 10.0 (CH_3), 22.4 (CH_2), 44.6 (N$-CH_3$), 56.5 (CH_2-N), 92.7, 94.6, 95.7 (ring *C*). MS (EI; *m/z* (relative intensity, %)): 639 (M^+, 4), 512 ($[M - I]^+$, 52), 58 ($Me_2NCH_2^+$, 100). Mp: 182 °C dec. Anal. Calcd for $C_{13}H_{22}I_2IrN$ (638.35): C, 24.42; H, 3.47; N, 2.19; I, 39.8. Found: C, 24.37; H, 3.60; N, 1.91; I, 39.7.

Complexes of **1** with an uncoordinated side chain (complexes **2** and **6**−**14**) are very difficult to purify. Neither recrystallization nor chromatography led to analytically pure samples. ^{1}H NMR spectra showing the nearly pure complexes are provided in the supplementary material.

Carbonyldiiodo[η^5-1-(2-(dimethylamino)ethyl)-2,3,4,5-tetramethylcyclopentadienyl]rhodium(III) (6). A solution of **4** in $CDCl_3$ was prepared in an NMR tube. Carbon monoxide was bubbled through this solution for 10 min. The NMR spectra were recorded using this sample. The IR spectrum was recorded on a CH_2Cl_2 solution prepared as described above. ^{1}H NMR ($CDCl_3$): δ 2.23, 2.24 (2s, 2 × 6H, CH_3), 2.25 (s, 6H, N$-CH_3$), 2.39 (t, br, J = 6.5 Hz, 2H, CH_2), 2.66 (t, br, J = 6.5 Hz, 2H, CH_2-N). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 11.4, 11.8 (CH_3), 23.9 (CH_2), 45.1 (N$-CH_3$), 58.7 (CH_2-N), 104.5, 105.5, 106.1 (ring *C*), 180.9 (d, J_{Rh-C} = 69 Hz, *C*O). IR (CH_2Cl_2): ν 2060 cm^{-1} (CO).

Carbonyldiiodo[η^5-1-(2-(dimethylamino)ethyl)-2,3,4,5-tetramethylcyclopentadienyl]iridium(III) (7). A 0.60-g (1.04-mmol) amount of **5** was dissolved in 40 mL of CH_2Cl_2. This solution was stirred for 2 h under an atmosphere of carbon monoxide. The reaction mixture was filtered and the residue extracted with 4 × 5 mL of CH_2Cl_2. The combined CH_2Cl_2 extracts were evaporated in vacuo, leaving 0.67 g (1.01 mmol, 97%) of **7** as a red-brown powder. ^{1}H NMR ($CDCl_3$): δ 2.18, 2.25 (2s, 2 × 6H, CH_3), 2.36 (s, 6H, N$-CH_3$), 2.55−2.67 (m, 4H, CH_2 and CH_2-N). ^{1}H NMR (C_6D_6): δ 1.53, 1.73 (2s, 2 × 6H, CH_3), 1.84 (s, 6H, N$-CH_3$), 1.90−1.98 (t, br, J = 6.7 Hz, 2H, CH_2), 2.21−2.26 (t, br, J = 6.7 Hz, 2H, CH_2-N). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 10.7, 11.4 (CH_3), 22.8 (CH_2), 44.6 (N$-CH_3$), 58.3 (CH_2-N), 97.5, 100.3, 102.1 (ring *C*), 163.5 (*C*O). IR (CH_2Cl_2): ν 2047 cm^{-1} (CO). MS (EI; *m/z* (relative intensity, %)): 639 ($[M - CO]^+$, 6), 512 ($[M - CO - I]^+$, 50), 471 ($[M - CO - I - C_3H_5N]^+$, 100), 58 ($Me_2NCH_2^+$, 84).

Photolysis of 7. A solution of **7** in C_6D_6 was irradiated at room temperature for 2 h in an NMR tube. The amount of **5** in the solution was determined by ^{1}H NMR spectroscopy.

Thermolysis of 7. A 0.28-g (0.42-mmol) amount of **7** was dissolved in 50 mL of toluene. The solution was heated to reflux for 4 h. After removal of the solvent in vacuo the composition of the solid residue was determined by ^{1}H NMR spectroscopy.

Diiodo[η^5-1-(2-(dimethylamino)ethyl)-2,3,4,5-tetramethylcyclopentadienyl](*tert*-butyl isocyanide)rhodium(III) (8). To a solution of 0.15 g (0.27 mmol) of **4** in 20 mL of CH_2Cl_2 was added dropwise 0.12 g (1.44 mmol) of *tert*-butyl isocyanide. The reaction mixture was stirred at room temperature for 2 h. The solution was filtered and the residue extracted with 3 × 4 mL of CH_2Cl_2. The combined CH_2Cl_2 extracts were evaporated in vacuo, leaving 0.15 g (0.24 mmol, 88%) of **8** as a brown powder. ^{1}H NMR ($CDCl_3$): δ 1.49 (s, 9H, CNC(CH_3)$_3$), 2.09, 2.11 (2s, 2 × 6H, CH_3), 2.24 (s, 6H, N$-CH_3$), 2.33 (t, br, J = 7.3 Hz, 2H, CH_2), 2.58 (t, br, J = 7.3 Hz, 2H, CH_2-N). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 11.1, 11.2 (CH_3), 23.0 (CH_2), 30.5 (CNC(CH_3)$_3$), 45.4 (N$-CH_3$), 58.3 (CN*C*(CH_3)$_3$), 58.9 (CH_2-N), 100.6−100.8 (m, ring *C*), 128.3 (*C*NC(CH_3)$_3$). IR (CH_2Cl_2): ν 2185 cm^{-1} (CN). MS (EI; *m/z* (relative intensity, %)): 549 ($[M - CNC(CH_3)_3]^+$, 1), 504 ($[M - I - 2H]^+$, 7), 422 ($[M - I - CNC(CH_3)_3 - H]^+$, 44), 377 ($[M - 2I - 2H]^+$, 18), 58 ($Me_2NCH_2^+$, 100).

Diiodo[η^5-1-(2-(dimethylamino)ethyl)-2,3,4,5-tetramethylcyclopentadienyl](*tert*-butyl isocyanide)iridium(III) (9). The preparation was analogous to that for **8**, yielding 0.10 g (0.13 mmol, 98%) of **9** as a brown powder. ^{1}H NMR ($CDCl_3$): δ 1.50 (s, 9H, CNC(CH_3)$_3$), 2.04, 2.11 (2s, 2 × 6H, CH_3), 2.29 (s, 6H, N$-CH_3$), 2.37−2.52 (m, 4H, CH_2 and CH_2-N). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 10.4, 11.3 (CH_3), 21.8 (CH_2), 31.0 (CNC(CH_3)$_3$), 43.9 (N$-CH_3$), 57.8 (CH_2-N), 58.3 (CN*C*(CH_3)$_3$), 88.5, 94.0, 97.5 (ring *C*), 117.5 (*C*NC(CH_3)$_3$). IR (CH_2Cl_2): ν 2173 cm^{-1} (CN). MS (EI; *m/z* (relative intensity, %)): 595 ($[M - I]^+$, 1), 510 ($[M - I - CNC(CH_3)_3 - 2H]^+$, 2), 384 ($[M - 2I - CNC(CH_3)_3 - H]^+$, 1), 58 ($Me_2NCH_2^+$, 100).

Diiodo[η^5-1-(2-(dimethylamino)ethyl)-2,3,4,5-tetramethylcyclopentadienyl](trimethylphosphine)rhodium(III) (10). To a solution of 0.16 g (0.29 mmol) of **4** in 20 mL of CH_2Cl_2 was added dropwise 0.12 g (1.50 mmol) of trimethylphosphine. The reaction mixture was stirred at room temperature for 1 h and then filtered. The solvent was evaporated in vacuo, leaving 0.15 g of a brown powder. This powder was extracted with 10 mL of benzene. After filtration and washing of the residue with 2 × 5 mL of benzene the filtrate was evaporated in vacuo, leaving 0.10 g (0.16 mmol, 55%) of **10** as a brown solid. ^{1}H NMR ($CDCl_3$): δ 1.83 (d, J_{P-H} = 10.8 Hz, 9H, P(CH_3)$_3$), 2.00 (d, J_{P-H} = 0.4 Hz, 6H, CH_3), 2.02 (d, J_{P-H} = 0.5, 6H, CH_3), 2.25 (s, 6H, N$-CH_3$), 2.29−2.34 (m, 2H, CH_2), 2.46−2.52 (m, 2H, CH_2-N). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 11.1 (CH_3), 20.5 (d, J_{P-C} = 36 Hz, P(CH_3)$_3$), 24.5 (CH_2), 45.4 (N$-CH_3$), 58.8 (CH_2-N), 99.1, 100.2 (ring *C*). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −2.4 (d, J_{Rh-P} = 135 Hz, P(CH_3)$_3$). MS (EI; *m/z* (relative intensity, %)): 498 ($[M - I]^+$, 79), 422 ($[M - I - P(CH_3)_3]^+$, 97), 58 ($Me_2NCH_2^+$, 100).

Diiodo[η^5-1-(2-(dimethylamino)ethyl)-2,3,4,5-tetramethylcyclopentadienyl](trimethylphosphine)iridium(III) (11). To a solution of 0.12 g (0.19 mmol) of **5** in 10 mL of CH_2Cl_2 was added dropwise 0.06 g (0.79 mmol) of trimethylphosphine. The reaction mixture was stirred at room temperature for 1 h. The solution was filtered and the residue extracted with 3 × 4 mL of CH_2Cl_2. The combined CH_2Cl_2 extracts were evaporated in vacuo, leaving 0.13 g (0.18 mmol, 96%) of **11** as a brown powder. ^{1}H NMR ($CDCl_3$): δ 1.90 (d, J_{P-H} = 10.6 Hz, 9H, P(CH_3)$_3$), 1.94 (d, J_{P-H} = 2.2 Hz, 6H, CH_3), 1.98 (d, J_{P-H} = 2.2 Hz, 6H, CH_3), 2.25 (s, 6H, N$-CH_3$), 2.30−2.43 (m, 4H, CH_2 and CH_2-N). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 10.5, 10.7 (CH_3), 19.0 (d, J_{P-C} = 43 Hz, P(CH_3)$_3$), 23.3 (CH_2), 44.8 (N$-CH_3$), 57.8 (CH_2-N), 90.8, 93.2, 93.6 (ring *C*). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −44.4 (P(CH_3)$_3$). MS (EI; *m/z* (relative intensity, %)): 715 (M^+, 3), 586 ($[M - I]^+$, 20), 58 ($Me_2NCH_2^+$, 100). High-resolution MS (EI; *m/z*): calcd (^{193}Ir), 714.9913; found, 714.9914.

Diiodo[η^5-1-(2-(dimethylamino)ethyl)-2,3,4,5-tetramethylcyclopentadienyl](triphenylphosphine)iridium(III) (12). To a solution of 0.22 g (0.34 mmol) of **5** in 20 mL of CH_2Cl_2 was added 0.09 g (0.34 mmol) of triphenylphosphine. The reaction mixture was stirred at room temperature for 45 min. The solution was filtered and the residue extracted with 10 mL of CH_2Cl_2. The combined CH_2Cl_2 extracts were evaporated in vacuo, leaving 0.24 g (0.27 mmol, 78%) of **12** as a red-brown powder. ^{1}H NMR ($CDCl_3$): δ 1.69 (d, J_{P-H} = 1.3 Hz, 6H, CH_3), 1.73 (d, J_{P-H} = 1.6 Hz, 6H, CH_3), 1.97−2.09 (m, 2H, CH_2), 2.20 (s, 6H, N$-CH_3$), 2.29−2.40 (m, 2H, CH_2-N), 7.43 (m, 6H, *o*- or *m-H* of PPh_3), 7.59 (m, 6H, *o*- or *m-H* of PPh_3), 7.74 (m, 3H, *p-H* of PPh_3). ^{13}C{^{1}H} NMR ($CDCl_3$):[17] δ 10.4, 10.5 (CH_3), 22.6 (CH_2), 44.8 (N$-CH_3$), 57.7 (CH_2-N), 92.8, 93.9, 95.3 (ring *C*). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −8.8 (PPh_3). MS (EI; *m/z* (relative intensity, %)): 512 ($[M - I - PPh_3]^+$, 9), 262 (PPh_3^+, 100), 58 ($Me_2NCH_2^+$, 35).

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(17) ^{13}C NMR signals for the coordinated triphenylphosphine are obscured by an impurity of free triphenylphosphine which could not be removed.

Dicarbonyl[η^5-1-(2-(dimethylamino)ethyl)-2,3,4,5-tetramethylcyclopentadienyl]rhodium(I) (13). A solution of 0.19 g (0.35 mmol) of **4** in 20 mL of THF was added to sodium amalgam (0.28 g (12 mmol) of Na, 30 g, 0.9%). After the reaction mixture was stirred for 1 h under an atmosphere of carbon monoxide, it was decanted from the amalgam. The solvent was removed in vacuo and the residue extracted with 10 mL of *n*-hexane. After filtration and washing of the residue with 2 × 5 mL of *n*-hexane the solvent was removed in vacuo, leaving 0.11 g (0.31 mmol, 90%) of **13** as a yellow-brown oil. ^{1}H NMR ($CDCl_3$): δ 2.00, 2.03 (2s, 2 × 6H, $\mathrm{C}H_3$), 2.22–2.28 (m, 2H, $\mathrm{C}H_2$), 2.28 (s, 6H, $\mathrm{N{-}C}H_3$), 2.42–2.53 (m, 2H, $\mathrm{C}H_2\mathrm{{-}N}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($CDCl_3$): δ 10.8, 10.9 ($C\mathrm{H}_3$), 23.3 ($C\mathrm{H}_2$), 45.4 ($\mathrm{N{-}}C\mathrm{H}_3$), 63.0 ($C\mathrm{H_2{-}N}$), 100.3, 101.3, 104.4 (3d, $J_{\mathrm{Rh-C}}$ = 4 Hz, ring *C*), 194.1 (d, $J_{\mathrm{Rh-C}}$ = 83 Hz, *C*O). IR (CH_2Cl_2): ν 1987, 1940 cm^{-1} (CO). MS (CI; *m/z* (relative intensity, %)): 323 ([M − CO]$^+$, 55), 295 ([M − 2CO]$^+$, 19), 293 ([M − Me_2NCH_2]$^+$, 97), 58 ($Me_2NCH_2^+$, 100). High-resolution MS (EI; *m/z*): calcd [M − CO]$^+$, 323.0756; found, 323.0754.

Dicarbonyl[η^5-1-(2-(dimethylamino)ethyl)-2,3,4,5-tetramethylcyclopentadienyl]iridium(I) (14). The preparation was analogous to that for **13**, yielding 0.30 g (0.68 mmol, 73%) of **14** as a coffee brown oil. ^{1}H NMR ($CDCl_3$): δ 2.15, 2.16 (2s, 2 × 6H, $\mathrm{C}H_3$), 2.19–2.26 (m, 2H, $\mathrm{C}H_2$), 2.27 (s, 6H, $\mathrm{N{-}C}H_3$), 2.54–2.60 (m, 2H, $\mathrm{C}H_2\mathrm{{-}N}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($CDCl_3$): δ 10.5, 10.6 ($C\mathrm{H}_3$), 23.2 ($C\mathrm{H}_2$), 45.4 ($\mathrm{N{-}}C\mathrm{H}_3$), 62.8 ($C\mathrm{H_2{-}N}$), 96.8, 97.8, 100.7 (ring *C*), 176.6 (*C*O). IR (CH_2Cl_2): ν 2018, 1936 cm^{-1} (CO). MS (EI; *m/z* (relative intensity, %)): 441 (M$^+$, 1), 413 ([M − CO]$^+$, 6), 58 ($Me_2NCH_2^+$, 100). High-resolution MS (EI; *m/z*): calcd (^{193}Ir), 441.1283; found, 441.1288.

[η^5:η^1-1-(2-(Dimethylamino)ethyl)-2,3,4,5-tetramethylcyclopentadienyl](oxalato)rhodium(III) (15). To a solution of 0.26 g (0.47 mmol) of **4** in 25 mL of CH_2Cl_2 was added 0.15 g (0.49 mmol) of silver oxalate. The reaction mixture (suspension) was stirred for 6 days at room temperature under exclusion of light. The solution was filtered and the residue extracted with 2 × 5 mL of CH_2Cl_2. The combined CH_2Cl_2 extracts were evaporated in vacuo, leaving 0.16 g (0.42 mmol, 89%) of **15** as a brown powder. ^{1}H NMR ($CDCl_3$): δ 1.60, 1.83 (2s, 2 × 6H, $\mathrm{C}H_3$), 2.34 (d, $J_{\mathrm{Rh-H}}$ = 0.8 Hz, 6H, $\mathrm{N{-}C}H_3$), 2.52 (t, *J* = 6.4 Hz, 2H, $\mathrm{C}H_2$), 3.66 (t, *J* = 6.4 Hz, 2H, $\mathrm{C}H_2\mathrm{{-}N}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($CDCl_3$): δ 8.5 ($C\mathrm{H}_3$), 22.8 ($C\mathrm{H}_2$), 49.8 ($\mathrm{N{-}}C\mathrm{H}_3$), 74.4 ($C\mathrm{H_2{-}N}$), 82.3 (d, $J_{\mathrm{Rh-C}}$ = 10 Hz, ring *C*), 98.2 (d, $J_{\mathrm{Rh-C}}$ = 6 Hz, ring *C*), 106.1 (d, $J_{\mathrm{Rh-C}}$ = 9 Hz, ring *C*), 166.0 (*C*=O). IR (CH_2Cl_2): ν 1678 cm^{-1} (C=O). Mp: 224–228 °C dec. Anal. Calcd for $C_{15}H_{22}NO_4Rh$ (383.25): C, 46.99; H, 5.79; N, 3.66. Found: C, 46.31; H, 6.53; N, 3.17.

[η^5:η^1-1-(2-(Dimethylamino)ethyl)-2,3,4,5-tetramethylcyclopentadienyl](oxalato)iridium(III) (16). To a solution of 0.30 g (0.47 mmol) of **5** in 25 mL of CH_2Cl_2 was added 0.14 g (0.47 mmol) of solid silver oxalate. The reaction mixture (suspension) was stirred for 4 days at room temperature under exclusion of light. The solution was filtered and the residue extracted with 10 mL of CH_2Cl_2. The combined CH_2Cl_2 extracts were evaporated in vacuo, leaving 0.21 g (0.44 mmol, 94%) of **16** as a brown powder. ^{1}H NMR ($CDCl_3$): δ 1.59, 1.71 (2s, 2 × 6H, $\mathrm{C}H_3$), 2.43 (s, 6H, $\mathrm{N{-}C}H_3$), 2.47 (t, *J* = 6.4 Hz, 2H, $\mathrm{C}H_2$), 3.77 (t, *J* = 6.4 Hz, 2H, $\mathrm{C}H_2\mathrm{{-}N}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($CDCl_3$): δ 8.6, 9.0 ($C\mathrm{H}_3$), 22.7 ($C\mathrm{H}_2$), 50.1 ($\mathrm{N{-}}C\mathrm{H}_3$), 71.6 (ring *C*), 78.9 ($C\mathrm{H_2{-}N}$), 90.0, 96.9 (ring *C*), 165.7 (*C*=O). IR (CH_2Cl_2): ν 1650 cm^{-1} (C=O). Mp: 218–222 °C dec. Anal. Calcd for $C_{15}H_{22}IrNO_4$ (472.56): C, 38.13; H, 4.69; N, 2.96. Found: C, 38.43; H, 4.76; N, 2.80.

[η^5-1-(2-(Dimethylamino)ethyl)-2,3,4,5-tetramethylcyclopentadienyl](oxalato)(trimethylphosphine)rhodium(III) (17). To a solution of 0.14 g (0.36 mmol) of **15** in 10 mL of CH_2Cl_2 was added 0.10 g (1.30 mmol) of trimethylphosphine. After 2 h of stirring at room temperature the reaction mixture was filtered. The resiude was washed with 2 × 5 mL of CH_2Cl_2. Removal of the solvent in vacuo yields 0.13 g (0.29 mmol, 81%) of **17** as a yellow-orange solid. ^{1}H NMR ($CDCl_3$): δ 1.40 (d, $J_{\mathrm{P-H}}$ = 11.0 Hz, 9H, $\mathrm{P(C}H_3)_3$), 1.66 (d, $J_{\mathrm{P-H}}$ = 3.3 Hz, 6H, $\mathrm{C}H_3$), 1.68 (d, $J_{\mathrm{P-H}}$ = 3.1 Hz, 6H, $\mathrm{C}H_3$), 2.22 (s, 6H, $\mathrm{N{-}C}H_3$), 2.21–2.38 (m, 4H, $\mathrm{C}H_2$ and $\mathrm{C}H_2\mathrm{{-}N}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($CDCl_3$): δ 8.9, 9.1 ($C\mathrm{H}_3$), 12.7 (d, $J_{\mathrm{P-C}}$ = 29 Hz, $\mathrm{P}(C\mathrm{H}_3)_3$), 22.7 ($C\mathrm{H}_2$), 45.4 ($\mathrm{N{-}}C\mathrm{H}_3$), 57.5 ($C\mathrm{H_2{-}N}$), 96.1, 97.9 (ring *C*), 166.0 (*C*=O). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($CDCl_3$): δ 5.3 (d, $J_{\mathrm{Rh-P}}$ = 156 Hz, $P(CH_3)_3$). IR (CH_2Cl_2): ν 1650 cm^{-1} (C=O). Mp: 68–70 °C. Anal. Calcd for $C_{18}H_{31}NO_4PRh$ (459.33): C, 47.05; H, 6.81; N, 3.05. Found: C, 46.04; H, 7.05; N, 2.59.

[η^5-1-(2-(Dimethylamino)ethyl)-2,3,4,5-tetramethylcyclopentadienyl](oxalato)(trimethylphosphine)iridium(III) (18). The preparation was analogous to that for **17**, yielding 0.16 g (0.29 mmol, 78%) of **18** as a yellow-tan solid. ^{1}H NMR ($CDCl_3$): δ 1.46 (d, $J_{\mathrm{P-H}}$ = 10.7 Hz, 9H, $\mathrm{P(C}H_3)_3$), 1.66 (d, $J_{\mathrm{P-H}}$ = 2.2 Hz, 6H, $\mathrm{C}H_3$), 1.71 (d, $J_{\mathrm{P-H}}$ = 1.9 Hz, 6H, $\mathrm{C}H_3$), 2.23–2.27 (m, 2H, $\mathrm{C}H_2$), 2.28 (s, 6H, $\mathrm{N{-}C}H_3$), 2.37–2.42 (m, 2H, $\mathrm{C}H_2\mathrm{{-}N}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($CDCl_3$): δ 8.9, 9.2 ($C\mathrm{H}_3$), 12.6 (d, $J_{\mathrm{P-C}}$ = 36 Hz, $\mathrm{P}(C\mathrm{H}_3)_3$), 22.7 ($C\mathrm{H}_2$), 45.3 ($\mathrm{N{-}}C\mathrm{H}_3$), 57.6 ($C\mathrm{H_2{-}N}$), 87.8, 91.0, 91.7 (ring *C*), 165.6 (*C*=O). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($CDCl_3$): δ −17.0 ($P(CH_3)_3$). IR (CH_2Cl_2): ν 1660 cm^{-1} (C=O). Mp: 70–72 °C. Anal. Calcd for $C_{18}H_{31}IrNO_4P$ (548.64): C, 39.33; H, 5.69; N, 2.55. Found: C, 39.40; H, 6.29; N, 2.37.

X-ray Structure Determination. A single crystal was fixed with polyurethane on a glass fiber for data collection. Crystallographic programs used for structure solution and refinement were from SHELXTL PLUS. The structure was solved by using direct methods and was refined by using full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms. All the hydrogen atoms were refined at calculated positions.

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Supplementary Material Available: Tables of additional bond distances and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for **4** and **5** and figures giving ^{1}H NMR spectra of the compounds **2** and **6**–**14** (16 pages). Ordering information is given on any current masthead page.

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