Syntheses of Ortho-Mercurated and -Palladated (η^6-Arene)tricarbonylchromium Complexes

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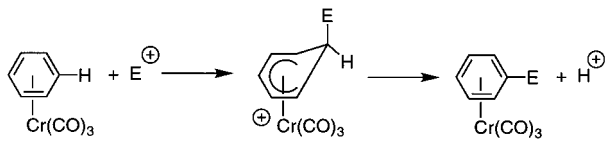
The selective ortho mercuration of tricarbonylchromium derivatives of 2-phenylpyridine, *N*,*N*-dimethylbenzylamine, (1*S*)-1-(dimethylamino)-1-phenylethane, and 2-phenyl-2-oxazoline by $Hg(OAc)_2$ is reported. The mercurations of the latter (η^6-arene)$Cr(CO)_3$ complexes bearing an endogenous ligand have been carried out in soft conditions with yields ranging from 13 to 83%. The optically active complex of (1*S*)-1-(dimethylamino)-1-phenylethane was stereoselectively orthomercurated. The conversion of the chloromercurated complexes, e.g. (η^6-Ar-HgX)$Cr(CO)_3$, into the corresponding homoleptic trinuclear [(η^6-Ar)$Cr(CO)_3$]$_2$Hg complexes was readily carried out by reaction with Me_4NCl in boiling acetone. In almost all cases, the so-called symmetrization reaction afforded a mixture of two diastereomers, except for the derivative of (1*S*)-1-(dimethylamino)-1-phenylethane, which afforded a unique "symmetrized" product. This result suggests that the "symmetrization" reaction occurred with retention of the configuration of the mercury-bound ipso carbon atom. The trimetallic and bimetallic mercurated (η^6-arene)$Cr(CO)_3$ complexes were readily converted into cyclopalladated binuclear complexes upon transmetalation with Pd(II) salts. The structures of two ortho-mercurated compounds and two ortho-palladated complexes are reported.

Introduction

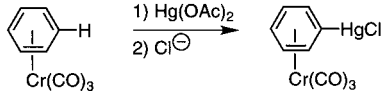
It is well-established that the $Cr(CO)_3$ moiety in (η^6-arene)tricarbonylchromium complexes decreases the electron density at the arene ligand.[1] This property has a direct effect on the electrophilicity of the arene ligand, which is considerably enhanced toward addition of nucleophiles. In contrast, the coordinated arene presumably displays poor or no reactivity toward electrophiles in so-called aromatic electrophilic substitution (S_EAr) reactions (Scheme 1).

A few examples of Friedel−Crafts type reactions carried out with (η^6-arene)$Cr(CO)_3$ complexes showed that the conversions were quite low and the regioselectivities somewhat poor.[2] As far as S_EAr reactions are concerned, only two reports describe the reaction of

Scheme 1



mercury(II) acetate, $Hg(OAc)_2$, with (η^6-arene)tricarbonylchromium complexes: for example, (η^6-benzene)$Cr(CO)_3$,[3] (η^6-toluene)$Cr(CO)_3$, and (η^6-*N*,*N*-dimethylaniline)$Cr(CO)_3$.[4] In all cases, the authors stated that the reaction worked fairly well with the benzene derivative (eq 1), while the toluene derivative reacted sluggishly



(1)

and, surprisingly, the aniline derivative afforded no product at all. Recent advances in the study of the mercuration of aromatics[5] indicate that this reaction must not be considered as a simple S_EAr type transformation entailing only the successive transient formation of π and σ complexes.[6] The actual process is more likely a balanced combination of the S_EAr process with a

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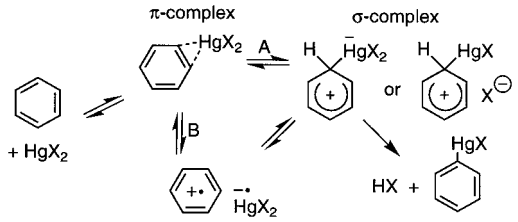
Scheme 2



second pathway that might involve light-promoted monoelectron transfers and charged radical intermediates resulting from the collapse of the initial transient π complex (Scheme 2).[7]

In light of this information we considered it worth revisiting the mercuration[8] by $Hg(OAc)_2$ of a series of model (η^6-arene)tricarbonylchromium complexes bearing an endogenous ligand and studying the synthetic usefulness of the binuclear products in further organometallic transformations. It is well-known indeed that orthomercuration occurs readily with aromatic substrates that possess endogenous Lewis bases.[9] Such ortho-mercurated aromatics are useful substrates for transmetalation reactions and are moreover interesting for the synthesis of cyclometalated complexes that are not accessible by "C−H activation"-based methods.[10]

Herein, we report on the selective ortho mercuration of tricarbonylchromium complexes of 2-phenylpyridine, *N*,*N*-dimethylbenzylamine, (1*S*)-1-(dimethylamino)-1-phenylethane and 2-phenyl-2-oxazoline. We also report on the conversion of the chloromercurated products, e.g. (η^6-Ar−HgX)$Cr(CO)_3$, into the corresponding homoleptic trinuclear [(η^6-Ar)$Cr(CO)_3$]$_2$Hg complexes and cyclopalladated binuclear complexes upon so-called symmetrization and transmetalation reactions, respectively.

Results and Discussion

Ortho Mercuration of Model (η^6-arene)$Cr(CO)_3$ Complexes. According to numerous reports, the preparation of metalated (η^6-arene)tricarbonylchromium complexes can be carried out by not less than six direct ways:[11] (1) low-temperature lithiation−deprotonation,[12,13] (2) ipso-S_NAr displacement of a halogen leaving group by a nucleophilic metal anion,[14] (3) C−H bond activation,[15] (4) oxidative addition of a metal to a C_{Ar}−X bond[16] and a Grignard type reaction,[17] (5) CO extrusion from a metal−acyl complex,[18] and, seldom reported, (6) electrophilic aromatic substitution or mercuration.[3]

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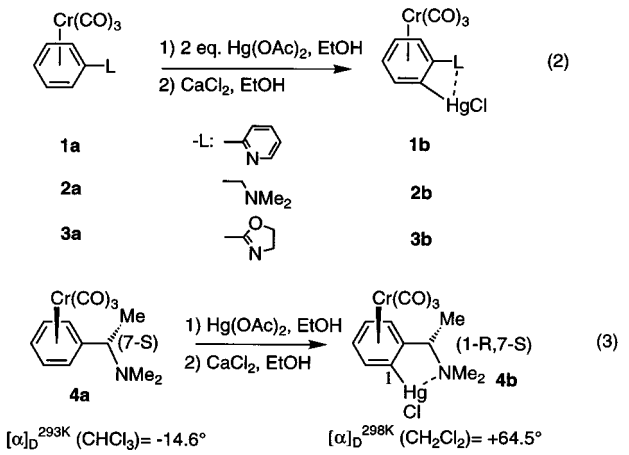
Regioselectivity in the metalation of (η^6-arene)tricarbonylchromium complexes arises from those classical effects that are readily encountered with organic aromatic substrates: i.e., electronic mesomeric/inductive effects as well as chelation or electrostatic interaction with the incoming metal center. For instance, ortho mercuration of non-π-coordinated aromatics is greatly favored with substrates that possess an endogenous σ-donor ligand, which supposedly interacts with mercury diacetate in the early stages of the mercuration reaction and presumably assists the electrophilic attack of the arene ring. The formation of a coordination adduct between the ligand and $Hg(OAc)_2$ is likely to be the kinetically limiting step.[9] As a consequence, the Lewis-type basicity of the endogenous base L should play a important role in the strength of the corresponding Hg−L bond and the resulting "electrophilicity" of the coordinated Hg(II) center.

We submitted compounds **1a**,[19] **2a**, and **3a** (eq 2) and compound **4a** (eq 3) to the action of a slight excess of $Hg(OAc)_2$ in EtOH for 3−4 h at 80 °C. Generally, in the



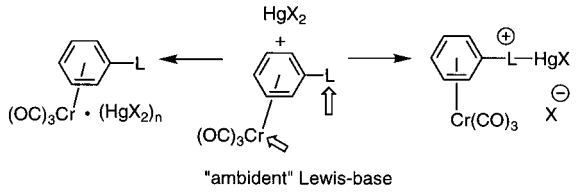
early stages of the experiment, i.e., shortly after total homogenization of the medium, a net color change from yellow to dark orange occurred. After $^1/_2$ h, an abundant off-white precipitate appeared and persisted until the end of the warming, at which point the solution became yellow-brown. Filtration of the mixture through Celite afforded a clear solution, which was treated with a saturated solution of $CaCl_2$ in EtOH. The chloromercurated product readily precipitated as a bright yellow solid. Yields and reaction conditions are listed in Table 1. The corresponding products did not display sensitivity to air either in the solid state or in solution. They were purified by conventional recrystallization or flash chromatography. In the case of **4a** ($[\alpha]_D(CHCl_3, 293\ K) = -14.6°$ ($c = 1.03$ g/100 mL)), the sole product recovered was the optically active complex **4b**. For the latter, although we were unfortunate in obtaining X-ray-suitable crystals, we assume that the mercuration took place similarly to other reported cases of stereoselective lithiation[12p] and manganation of **4a**,[20] i.e., at the ortho position, implying a lower steric hindrance between the $Cr(CO)_3$ rotor and the methyl group attached to the benzylic atom, where the latter two are in a trans relationship (eq 3).

Table 1. Mercuration of 1a, 2a, 3a, and 4a: Experimental Conditions and Yields of Products 1b, 2b, 3b, and 4b

entry	reagent	substrate	*T* (°C)	reacn time (h)	product (yield (%))
1	$Hg(OCOCH_3)_2$	**1a**	20	1	**1b** (30)
2	$Hg(OCOCH_3)_2$	**1a**	50	1	**1b** (83)
3	$Hg(OCOCH_3)_2$	**1a**	80	1	**1b** (82)
4	$Hg(OCOCH_3)_2$	**1a**	80	4	**1b** (85)
5	$Hg(OCOCF_3)_2$	**1a**	20	1	no reacn
6	$Hg(OCOCH_3)_2$	**2a**	80	3	**2b** (38)
7	$Hg(OCOCH_3)_2$	**2a**	80	15	**2b** (35)
8	$Hg(OCOCF_3)_2$	**2a**	60	1.5	dec
9	$Hg(OCOCH_3)_2$	**3a**	80	3	**3b** (17)
10	$Hg(OCOCH_3)_2$	**4a**	80	3	**4b** (47)

Optimization of the mercuration of **1a** was attempted by restricting the reaction time to 1 h and by varying the temperature of the medium. We observed that the introduction of acetic acid in the medium did not significantly affect the yield of mercurated product. We found that a conversion of 83% in **1b** could be readily reached at 50 °C after 1 h of reaction (Table 1, entry 2). Carrying out the reaction at 20 °C afforded a lower conversion of 30% (Table 1, entry 1). Attempts at ortho mercuration using the more electrophilic reagent $Hg(OC(O)CF_3)_2$ were not successful (Table 1, entry 5). In one case, heating a mixture of **2a** and the latter mercury salt in ethanol even resulted in the fast decomposition of the (η^6-arene)tricarbonylchromium substrate and in the formation of greenish solids mixed to metallic mercury. The reaction of $Hg(OC(O)CF_3)_2$ with **1a** in CH_2Cl_2 at room temperature afforded two adducts, possibly in equilibrium. The one in solution resulted presumably from an interaction of the $Cr(CO)_3$ fragment with the mercury(II) center of $Hg(OC(O)CF_3)_2$: it displayed a set of two bands at 2030 and 1969 cm^{-1} and at 1662 cm^{-1} (Table 2, entry 5). According to the studies of Lewis,[21] Magomedov,[22] and Lokshin[23] on the IR spectroscopic properties of (η^6-arene)$M(CO)_3 \cdot n HgX_2$ adducts, the CO stretching bands of the $M(CO)_3$ moiety undergo a significant shift toward higher energies and a net change of their vibration mode upon interaction with HgX_2 Lewis-type acids. One must note that mercury(II) salts may interact with the $Cr(CO)_3$ fragment and the substrates addressed here may be considered as potential ambident[24] Lewis-type bases with basic sites both at the nitrogen atom and at the $Cr(CO)_3$ fragment (Scheme 3). The other insoluble adduct pre-

Scheme 3



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(23) Lokshin, B. V.; Rusach, E. B.; Kolobova, N. E.; Makarov, Yu. V.; Ustynyuk, N. A.; Zdanovich, V. I.; Zhakaeva, A. Zh.; Setkina, V. N. *J. Organomet. Chem.* **1976**, *108*, 353.

Table 2. Study of the Interaction of Mercury(II) Trifluoroacetate with Complex 1a by IR Spectroscopy in Solution and KBr

entry	sample	conditions	IR sample	ν(CO) (cm^{-1})	ν(C=O) (cm^{-1})
1	**1a**		CH_2Cl_2	1970, 1896	
2	**1a**		KBr	1947, 1871	
3	$Hg(OC(O)CF_3)_2$		CH_2Cl_2		1711, 1672 (w)
4	$Hg(OC(O)CF_3)_2$		KBr		1670, 1600 (w)
5	**1a** + $Hg(OC(O)CF_3)_2$	30 min reflux in CH_2Cl_2, liquor	CH_2Cl_2	2030, 1969	1662
6	**1a** + $Hg(OC(O)CF_3)_2$	30 min reflux in CH_2Cl_2, yellow precipitate	KBr	1963, 1880	1682

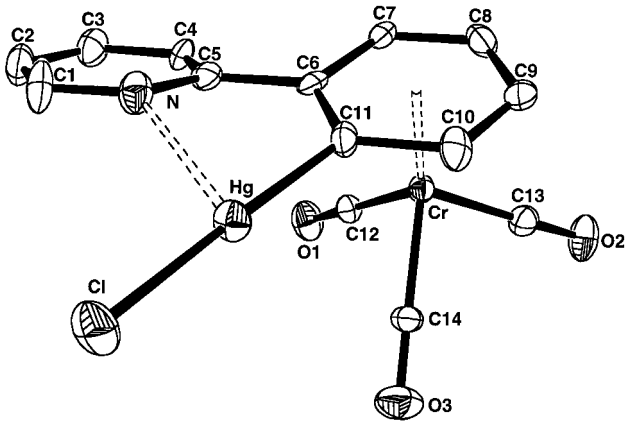


Figure 1. ORTEP diagram of the structure of **1b**. The ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å): Cr−C6, 2.226(6); Cr−C7, 2.210(8); Cr−C8, 2.217(8); Cr−C9, 2.223(8); Cr−C10, 2.228(8); Cr−C11, 2.245(9); Hg−C11, 2.071(9); Hg−Cl, 2.307(9); Hg−N, 2.670(9). Selected interatomic angles (deg): C14−Cr−C13, 88.5(4); C14−Cr−C12, 88.2(3); C12−Cr−C13, 89.5(3); C4−Hg−Cl, 130.6(4). Dihedral angle: C4−C5−C6−C7, 20.6(4).

cipitated out from CH_2Cl_2 as a yellow amorphous powder. Although we did not proceed to its complete characterization, it seemingly resulted from coordination of the Hg(II) center to the pyridyl nitrogen: an IR spectrum in KBr revealed two bands at 1963 and 1880 cm^{-1}, ascribed to a new (η^6-arene)$Cr(CO)_3$ species, and one intense band at 1682 cm^{-1} (Table 2, entry 6).

This yellow amorphous powder could be easily dissolved by treatment with a concentrated solution of $CaCl_2$ in absolute ethanol with formation of an off-white solid, presumably $HgCl_2$. Further analyses of the resulting yellow solution by means of ^1H NMR spectroscopy, after filtration and evaporation of the solvents, revealed the presence of only **1a**.

Structure of 2-[(η^6-2-(Chloromercurio)phenyl)-tricarbonylchromium]pyridine (1b). Complex **1b** was successfully recrystallized from dichloromethane and hexane to afford crystals of satisfactory quality. To our knowledge, the ORTEP diagram shown in Figure 1 is the first reported structure of a chloromercurated (η^6-arene)tricarbonylchromium complex. Table 3 lists the acquisition and refinement data for all the X-ray analyses reported herein. Compound **1b** crystallized in the triclinic system, and the lattice fits the $P\bar{1}$ space group. The caption of Figure 1 presents a list of selected interatomic distances and angles. The ring formed by C6, C7, C8, C9, C10, and C11 is nearly planar, as no significant deviations from the corresponding mean plane P_1 was noticed. In addition, the chromium atom is at an average distance of 2.23 Å from each of the arene carbon atoms. A torsion angle of 21.7° between P_2, which is formed by atoms N, C1, C2, C3, C4, and C5, and P_1 suggests that the interaction between the doublet of electrons of the nitrogen atom and the mercury(II) center is not optimal. The interatomic distance between the latter atoms is slightly longer than that observed by Constable, Tocher, and co-workers in the structure of the mononuclear chloromercurated 2-phenylpyridine complex.[10a]

"Symmetrization" of Ortho-Chloromercurated (η^6-arene)$Cr(CO)_3$ Complexes. It is well-known that under reducing conditions the chloromercurated substrate R−HgCl may convert into the so-called "symmetrized" R−Hg−R product.[25] The "symmetrization" reaction may be carried out in the presence of either inorganic reducing agents such as $Na_2S_2O_3$ and $Na_2[Sn(OH)_4]$ in water/organic solvent solutions or biphasic media or potential ligands of Hg(II) such as NH_3, amines, phosphines, etc.[26] Mechanistic studies showed that the rate of the "symmetrization" reaction might depend on the ability of R−Hg−X to dissociate into the ion pair $R-Hg^+,X^-$.[27] Therefore, the "symmetrization" reaction is expected to be greatly favored with loosely bound X^- ions in solvents of high dielectric constant, in the presence of a nucleophilic auxiliary, and with the assistance of a mercury-chelating agent such as EDTA, for instance. Vicente and co-workers have demonstrated in a series of reports related to the reactivity of various chloromercuric aryl derivatives that the "symmetrization" reaction could be done efficiently with the help of Me_4N^+,Cl^- in aprotic solvents of high dielectric constant.[28] Indeed, in this case the driving force of the reaction seemingly is the precipitation of the thermodynamically stable hexachlorobismercurate salt, i.e., $(Me_4N^+)_2Hg_2Cl_6^{2-}$. We applied this method to complexes **1b** and **2b** (eq 4) and to **4b** (eq 5), which were reacted with Me_4N^+,Cl^- in dry and boiling acetone. After several

(24) The term "ambident" generally refers to Brønsted-type substrates—acidic or basic in character—that possess two chemically different reactive sites susceptible of an acid−base type interaction. Herein, we extend the meaning of the term to Lewis-type substrates. See: Kornblum, N.; Seltzer, R.; Haberfield, P. *J. Am. Chem. Soc.* **1963**, *85*, 1148.

(25) Gilman, H.; Wright, G. F. *J. Am. Chem. Soc.* **1933**, *55*, 3302.

(26) (a) Sand, J. *Ber. Dtsch. Chem. Ges.* **1901**, *34*, 2906. (b) Todhunter, J. A.; Currell, D. L. *J. Org. Chem.* **1975**, *40*, 1362. (c) Kovar, R. F.; Rausch, M. D. *J. Org. Chem.* **1973**, *38*, 1918.

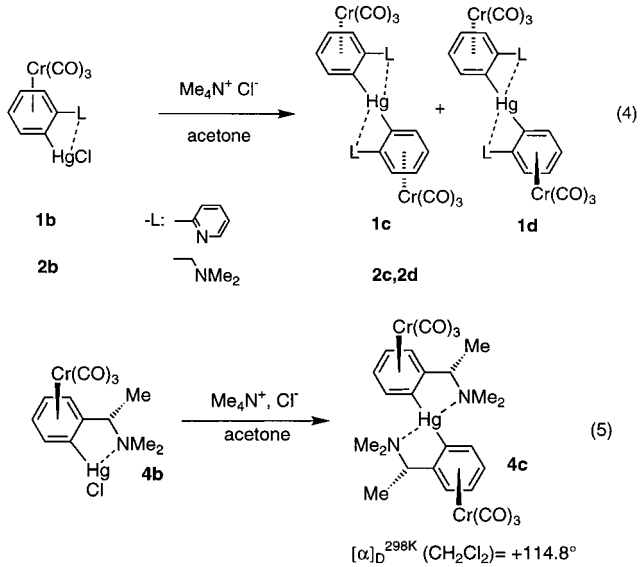
(27) Halpern, Y.; Garti, N. *J. Organomet. Chem.* **1975**, *92*, 291.

(28) (a) Vicente, J.; Chicote, M. T.; del Carmen Ramirez de Arellano, M.; Pelizzi, G.; Vitali, F. *J. Chem. Soc., Dalton Trans.* **1990**, 279. (b) Vicente, J.; Abad, J. A.; Gil-Rubio, J.; Jones, P. G.; Bembenek, E. *Organometallics* **1993**, *12*, 4151. (c) Vicente, J.; Abad, J. A.; Fernandez de Bobadilla, R.; Jones, P. G.; Ramirez de Arellano, M. C. *Organometallics* **1996**, *15*, 24. (d) Vicente, J.; Bermudez, M. D.; Carrion, F. J.; Jones, P. G. *Chem. Ber.* **1996**, *129*, 1395. (e) Vicente, J.; Abad, J. A.; Shaw, K. F.; Gil-Rubio, J.; del Carmen Ramirez de Arellano, M.; Jones, P. G. *Organometallics* **1997**, *16*, 4557. (f) Vicente, J.; Abad, J. A.; Rink, B.; Hernandez, F. S.; del Carmen Ramirez de Arellano, M. *Organometallics* **1997**, *16*, 5269.

Table 3. Listing of Acquisition and Refinement Data for X-ray Diffraction Analyses of Compounds 1b, 1c, 1i, and 1j

	1b	1c	1i	1j
formula	$C_{14}H_8ClCrHgNO_3$	$C_{28}H_{16}Cr_2HgN_2O_6$	$C_{19}H_{13}ClCrN_2O_3Pd{\cdot}CH_2Cl_2$	$C_{28}H_{16}Cr_2N_2O_6Pd{\cdot}CH_2Cl_2$
mol wt	526.26	781.03	596.11	771.77
cryst syst	triclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$C2/c$	$P2_1/c$	$P\bar{1}$
a (Å)	8.1124(5)	17.5518(7)	13.9929(7)	10.5039(3)
b (Å)	8.7029(4)	11.6574(5)	8.6166(2)	12.1316(4)
c (Å)	10.4643(5)	13.0084(6)	18.678(1)	22.9632(9)
α (deg)	81.940(5)			85.798(5)
β (deg)	76.274(5)	106.171(5)	104.620(5)	79.439(5)
γ (deg)	83.148(5)			81.390(5)
V (Å^3)	707.76(8)	2556.3(4)	2179.2(2)	2841.0(2)
Z	2	4	4	4
color	yellow	yellow	yellow	orange
cryst dimens (mm)	0.16 × 0.14 × 0.10	0.10 × 0.10 × 0.08	0.18 × 0.10 × 0.04	0.16 × 0.08 × 0.02
ρ_{calcd} (g cm^{-3})	2.47	2.03	1.82	1.80
F_{000}	488	1496	1176	1528
μ (mm^{-1})	11.795	6.873	1.716	1.613
temp (K)	173	173	294	294
λ (Å)			0.710 73	
radiation			Mo Kα, graphite monochromated	
diffractometer			KappaCCD	
scan mode			"ϕ scans"	
hkl limits	−10 to +10/−11 to +11/−13 to +13	−22 to +22/−14 to +13/−16 to +16	−18 to +18/−11 to +8/−24 to +24	0−13/−15 to +15/−29 to +29
θ limits (deg)	2.5−27.50	2.5−27.48	2.5−27.50	2.5−27.50
no. of data measd	4583	4865	9017	12 924
no. of data with $I > 3\sigma(I)$	2612	2602	2853	7122
no. of variables	190	177	289	757
R	0.043	0.022	0.032	0.045
R_w	0.057	0.027	0.037	0.064
GOF	1.016	0.941	1.024	1.170
largest peak in final diff map (e Å^{-3})	2.155	1.725	0.409	0.757

hours of reactions, the "symmetrized" products could be isolated by classical chromatographic techniques.

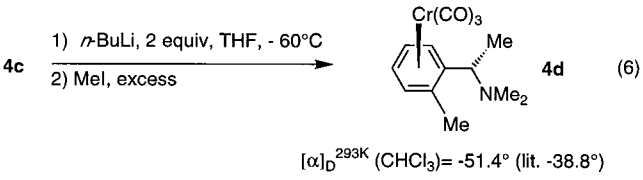


(4)

(5)

Ortho and meta heterodisubstituted (η^6-arene)tricarbonylchromium complexes possess intrinsic planar "metallocenic-like" asymmetry.[29] From our standpoint this peculiar property could complicate the analysis of the products of the "symmetrization" reaction, as for each substrate undergoing "symmetrization" two diastereomers could be expected. Complex **4b** was, however, an exception. Indeed, the latter reacted in boiling acetone with Me_4N^+,Cl^- to afford the single product **4c** possessing a specific rotation $[\alpha]^{298K}$ at 589 nm of about double the value of that measured for **4b** (eq 5). If one assumes that the empirical van't Hoff[30] principle of additivity of specific rotations is verified in the case of **4c**, i.e., $[\alpha]_{4c} \approx 2[\alpha]_{4b}$, this result strongly suggests that the "symmetrization" reaction took place with retention of configuration at the ipso carbon bearing the Hg(II) atom.

To further assess the stereochemistry of compound **4c**, we submitted it to a stoichiometric amount of *n*-BuLi (2 equiv per Hg) at −78 °C in THF (eq 6). The reaction



(6)

mixture was slowly warmed to −60 °C and stirred for 4.5 h at that temperature to enable the transmetalation reaction and the clean replacement or Hg by Li. Addition of an excess amount of MeI and warming of the reaction medium to room temperature afforded compound **4d**, i.e., (1*R*,7*S*)-(η^6-2,7-dimethyl-*N*,*N*-dimethylbenzylamine)tricarbonylchromium, which was obtained in 29% yield after chromatographic purification. The levorotatory property of **4d** was confirmed by a specific rotation $[\alpha]_D(CHCl_3, 293\ K)$ of −51.4° (c = 1.03 g/100 mL), a value close to that claimed for the same compound by Davies and co-workers[12m] ($[\alpha]_D(CHCl_3, 292\ K)$

(29) (a) Solladié-Cavallo, A. *Adv. Met. Org. Chem.* **1989**, *1*, 99. (b) Schlögl, K. *Top. Stereochem.* **1967**, *1*, 39.

(30) Eliel, E. L.; Wilen, S. H.; Mander, L. N. *Stereochemistry of Organic Compounds*; Wiley-Interscience: New York, 1994; p 1081.

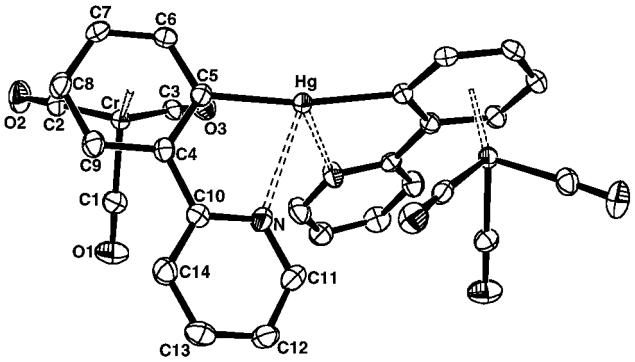


Figure 2. ORTEP diagram of the structure of **1c**. The ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å): Cr−C4, 2.244(3); Cr−C5, 2.270(4); Cr−C6, 2.233(3); Cr−C7, 2.237(3); Cr−C8, 2.232(4); Cr−C9, 2.214-(4); Hg−C5, 2.103(4); Hg−N, 2.608(5). Selected interatomic angles (deg): C1−Cr−C3, 86.5(2); C1−Cr−C2, 86.7(2); C2−Cr−C3, 86.7(2); C5−Hg−C5′, 169.6(2); N−Hg−N′, 76.4(2). Dihedral angle (deg): C9−C4−C10−C14, 9.5(2).

$= -38.8°$ ($c = 1.03$ g/100 mL)). This result supports the stereochemistry proposed above for complex **4c**.

As **1b** and **2b** were racemates, the "symmetrization" reaction produced in both cases pairs of diastereomers. Indeed, compounds **1c** and **1d** as well as **2c** and **2d** were recovered as mixtures with respective ratios of 2.33:1 and 1.5:1 and conversions of 90% and 67% (eq 4). Compounds **1c** and **1d** were submitted to fractional recrystallizations that unfortunately did not afford a pure aliquot but rather a sample enriched with **1c** that was used for further crystallographic and spectroscopic analyses. Complexes **2c** and **2d** as well as **4c** were found to be more light- and air-sensitive in solution and much less prone to withstand frequent recrystallizations without displaying signs of decomposition.

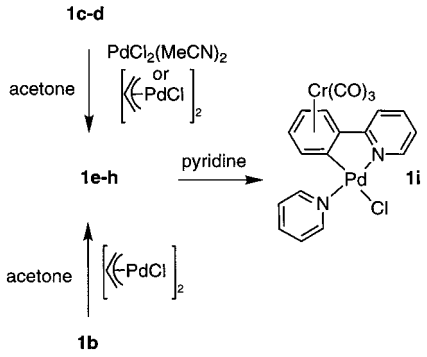
Structure of *lk-trans*-Bis[2-{(η^6-phenyl-κC^1)tricarbonylchromium(0)}pyridine-κN]mercury(II) (1c).[31] The structure of complex **1c** presents a C_2 axis of symmetry perpendicular to the C5−Hg−C5′ segment and in the plane formed by the atoms N, Hg, and N′ (Figure 2). In this trimetallic molecule the coordinated arene ring is planar. The two arene rings are twisted by an angle of 79.6°. A value of 10.6° is found for the torsion angle between the pyridyl and aryl rings. The central Hg(II) atom seemingly interacts with the two N atoms of the vicinal pyridyl fragments in an unusual non-square-planar environment characterized by a value of 76.4° for the angle N−Hg−N′. The structure of **1c** as described here is far more distorted than that of bis-[(η^6-phenyl)tricarbonylchromium]mercury(II) reported in the early 1980s by Kuz'mina and Strutchkov.[32a] In the latter complex the C_{ipso}−Hg−C_{ipso} angle amounts to 180°. In **1c**, the angle C5−Hg−C5′ is 169.6°, which is 10° less than in $[(C_6H_5)Cr(CO)_3]_2Hg$[32a] and bis[2-phenylpyridine- $\kappa C^{2'},\kappa N$]mercury(II).[32b]

Synthesis of the First Cyclopalladated (η^6-Arene)-tricarbonylchromium Complexes. Our first attempts to synthesize ortho-palladated (η^6-arene)tricarbonylchromium complexes by the so-called "C−H activation"[33] routes that entail either the direct reaction of inorganic Pd(II) salts[34] or the proton-catalyzed exchange of ligands of Pd(II) chelates[35] resulted in an unavoidable decomposition of the chromium(0) derivatives. Indeed, as far as the $Cr(CO)_3$ integrity is concerned, these methods failed to proceed in a nondestructive way with (η^6-arene)-$Cr(CO)_3$ complexes. The oxidative-addition route introduced for the first time by Basset,[16] Mortreux,[36] and coworkers with (η^6-halogenobenzene)$Cr(CO)_3$ and subsequently tested by us with various *o*-bromo-*N*,*N*-dimethylbenzylamine complexes did not yield any isolable product.

Hence, our results with the mercuration of (η^6-arene)-tricarbonylchromium encouraged us to check out the "transmetalation route" as a third reasonable alternative toward the preparative synthesis of a new class of cyclopalladated compounds. The transmetalation of arylmercury compounds is a well-known method for the synthesis of cyclopalladated aromatics.[37]

To test the feasibility of the transpalladation, we first submitted a mixture of complexes **1c** and **1d** to a stoichiometric amount of $Pd(MeCN)_2Cl_2$ (calculated vs Hg) at −15 °C (Scheme 4). Under these conditions, we

Scheme 4



were expecting that roughly only half of the starting Ar−Hg−Ar species would effectively react to give a palladacyclic complex. The reaction mixture was carefully warmed to room temperature for several hours in order to avoid the competing fast redox reaction between the (η^6-arene)$Cr(CO)_3$ and the Pd(II) salt. The resulting dark red solution, possibly containing the four organopalladium stereoisomers **1e**−**h** (Chart 1) and the chloromercurated byproduct **1b**, was subsequently filtered to remove the greenish suspension produced by a partial decomposition of the reactants. After addition of an excess of pyridine to the filtrate,[38] the resulting "monomerized" product, i.e. **1i**, could be recovered in 58% yield.

(31) In this article, we use the "*ul*" and "*lk*" descriptors of the so-called Seebach−Prelog system to describe the prochirality at the arene carbon atom σ-bonded to the metal atom: Seebach, D.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 654.

(32) (a) Kuz'mina, L. G.; Strutchkov, Yu. T. *Koord. Khim.* **1982**, *8*, 1542. (b) Black, S. C.; Deacon, G. B.; Edwards, G. L.; Gatehouse, B. M. *Aust. J. Chem.* **1993**, *46*, 1323.

(33) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403.

(34) (a) Cope, A. C.; Friedrich, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 909. (b) Thompson, J. M.; Heck, R. F. *J. Organomet. Chem.* **1975**, *40*, 2667. (c) Ryabov, A. D. *Synthesis* **1985**, 233.

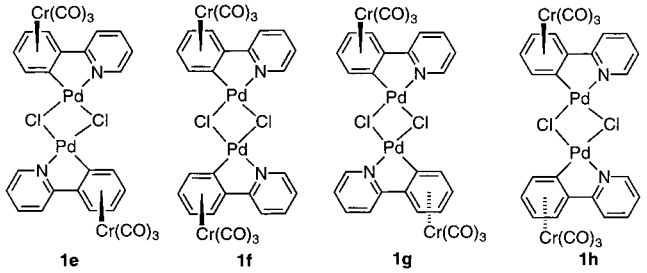
(35) Ryabov, A. D.; Yatsimirsky, A. K. *Inorg. Chem.* **1984**, *23*, 789. (b) Granell, J.; Sainz, D.; Sales, J.; Solans, X.; Font-Altaba, M. *J. Chem. Soc., Dalton Trans.* **1986**, 1785. (c) Ryabov, A. D. *Inorg. Chem.* **1987**, *26*, 1252.

(36) Carpentier, J. F.; Petit, F.; Mortreux, A.; Dufaud, V.; Basset, J. M.; Thivolle-Cazat, J. *J. Mol. Catal.* **1993**, *81*, 1.

(37) Constable, E. C.; Cargill Thompson, A. M. W.; Leese, T. A.; Reese, D. G. F.; Tocher, D. A. *Inorg. Chim. Acta* **1991**, *182*, 93.

(38) Ryabov, A. D.; Kuz'mina, L. G.; Polyakov, V. A.; Kazankov, G. M.; Ryabova, E. S.; Pfeffer, M.; van Eldik, R. *J. Chem. Soc., Dalton Trans.* **1995**, 999.

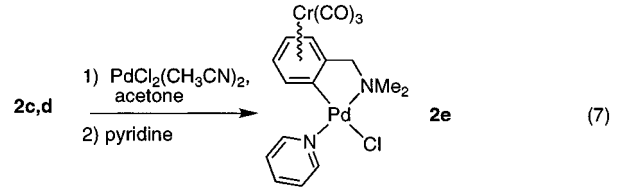
Chart 1



In a subsequent experiment we attempted the isolation of the four possible stereoisomers **1e**−**h** by low-temperature chromatography in a jacketed glass column.

We first eluted a large yellow fraction consisting essentially of complex **1b**. Two other red-orange fractions were also separated and analyzed by NMR techniques. The spectra showed that the fractions consisted of a mixture of more than two components each, which motivated us not to proceed to further purification attempts. We however confirmed that upon treatment with pyridine all the components of each chromatographic fraction converted into complex **1i**.

We found that the transpalladation reaction could be carried out with less side decomposition by reacting the Ar_2Hg substrates with $[(\eta^3\text{-allyl})PdCl]_2$ (Scheme 4). An experiment ran with a mixture of **1c** and **1d** in the presence of a stoichiometric amount of the latter Pd(II) complex afforded **1i** in 37% yield. We further checked the reactivity of $[(\eta^3\text{-allyl})PdCl]_2$ versus **1b** and were able to isolate complex **1i** in 54% yield. Complex **2e** (eq 7) could be obtained in 33% yield following a similar treatment of a mixture of complexes **2c** and **2d** with $PdCl_2(MeCN)_2$ and a subsequent "monomerization" by a reaction with an excess of pyridine.



(7)

Structures of (*SP*-4-4)-Chloro(pyridine)[{2-(η^6-phenyl-$\kappa C^{1'}$)tricarbonylchromium(0)}pyridine-κN^1]-palladium(II)[39] (1i) and *ul-cis*-Bis[{2-(η^6-phenyl-$\kappa C^{1'}$)-tricarbonylchromium(0)}pyridine-κN]palladium(II) (1j).[31] A raw sample of complex **1i** was submitted to crystallization in CH_2Cl_2 and hexane. Two classes of crystals were obtained: a set of dark orange crystals representing about 5% in mass of the solid mixture and a major set of orange-yellow crystals. The latter was firmly identified as **1i**, thanks to a X-ray diffraction study. The former unexpected complex was later identified as the homoleptic trinuclear complex **1j** (Chart 2).

Complex **1i** crystallized in the monoclinic system, and its crystal lattice fits the $P2_1/c$ space group. The structure of **1i**, which is given in Figure 3, presents no major distortions. The two connected aromatic rings are almost coplanar: the C11−C10−C9−C8 dihedral angle is 3.4(6)°. The C4−Pd distance is similar to those

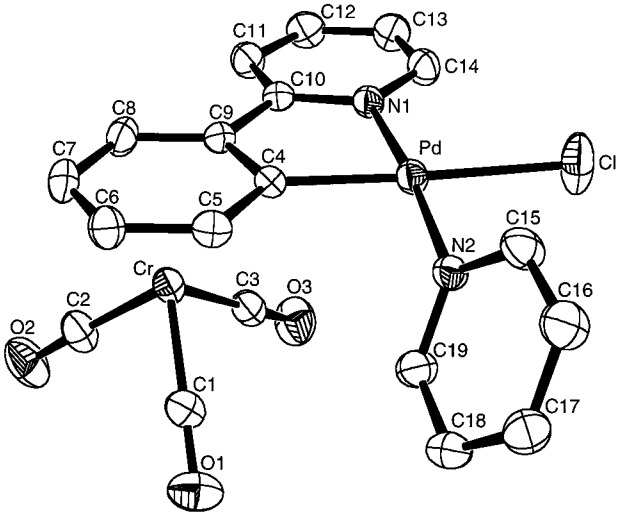
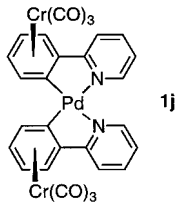


Figure 3. ORTEP diagram of the structure of **1i**. Ellipsoids are drawn at the 30% probability level. Hydrogen and solvent atoms have been omitted for clarity. Selected interatomic distances (Å): Cr−C4, 2.270(4); Cr−C5, 2.233(4); Cr−C6, 2.227(4); Cr−C7, 2.227(4); Cr−C8, 2.227(4); Cr−C9, 2.227(4); Pd−C4, 1.973(4); Pd−N1, 2.030(3); Pd−Cl, 2.376(1); Pd−N2, 2.032(3). Selected interatomic angles (deg): C3−Cr−C2, 88.3(2); C3−Cr−C1, 88.9(2); C1−Cr−C2, 86.2(2); C4−Pd−N1, 81.2(1); C4−Pd−Cl, 177.0(1); N1−Pd−N2, 174.0(1). Dihedral angle (deg): C11−C10−C9−C8, 3.4(1).

Chart 2



frequently encountered in similar "monomerized" Pd(II) complexes.[40] The Cr−C4 distance is only slightly longer than the average of the Cr−C_{Ar} distances as a result of either a weak electron-donating effect[41] of the Pd(II) center or a limited steric interaction with the surroundings of the Pd(II) center. It is worth noting that the Cr-bonded arene ring displays no significant out-of-mean-plane distortions.

Complex **1j** is a new example of homoleptic *cis*-Pd(II) chelate, numerous examples of which have been already reported.[42] In our case, the formation of such species was seemingly purely incidental, as all our subsequent attempts at synthesizing it on higher scales failed so far. We felt it essential, however, to report on this crystal structure, as it presents some interesting pecu-

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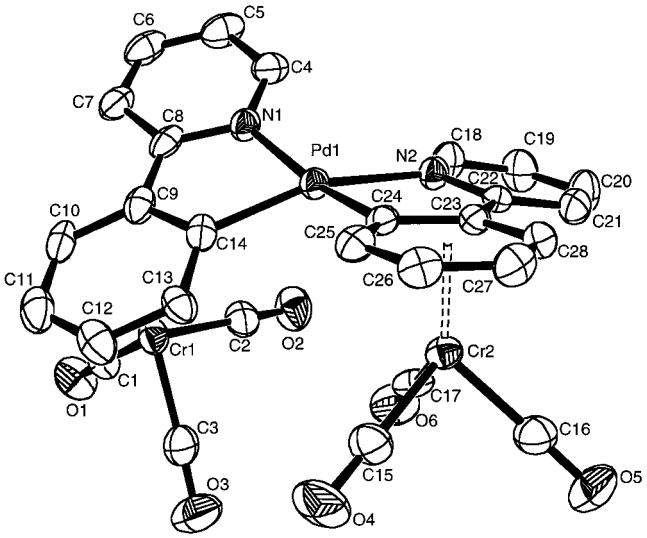

Figure 4. ORTEP diagram of the structure of **1j**. Half of the asymmetric unit is shown for clarity purposes. The ellipsoids are drawn at the 30% probability level. Hydrogen and solvent atoms have been omitted for clarity. Selected interatomic distances (Å): Cr1−C14, 2.293(5); Cr1−C13, 2.236(6); Cr1−C12, 2.196(6); Cr1−C11, 2.231(7); Cr1−C10, 2.183(6); Cr1−C9, 2.200(6); Pd−C14, 1.999(6); Pd−N1, 2.121(5); Pd−C24, 1.982(6); Pd−N2, 2.109(5); C13−C25, 3.297(6); C4−C18, 3.435(6). Selected interatomic angles (deg): C3−Cr1−C2, 90.4(3); C3−Cr1−C1, 88.4(3); C1−Cr1−C2, 86.7(3); C14−Pd−N2, 160.2(2); N1−Pd−C24, 167.9(2). Dihedral angle (deg): C7−C8−C9−C10, 9.1(2).

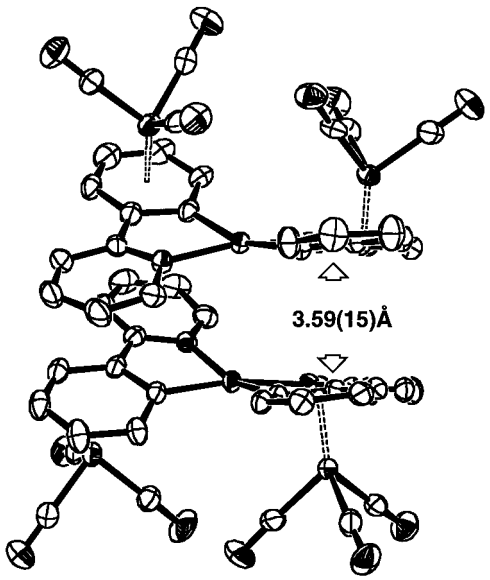

Figure 5. ORTEP diagram of the asymmetric unit of the crystal of **1j** with indication of the interplanar distance separating two molecules. The ellipsoids are drawn at the 30% probability level. Atoms of hydrogen and solvent have been omitted for clarity purposes.

liarities. Complex **1j** crystallized in the triclinic system, and the crystal lattice fits the $P\bar{1}$ space group. The asymmetric unit encompasses two molecules of **1j**. For clarity purposes only one has been arbitrarily displayed in Figure 4. Figure 5 presents a side view of the stacking of the two molecules in the asymmetric unit and an averaged value of the intermolecular/interplanar distance between two Pd(II)−chelate planes. The Pd−Pd interatomic distance is 3.739(6) Å. The feature that attracted our attention is the nonplanarity of the coordination environment of the Pd(II) center consisting of atoms C14, N1, N2, and C24 (Figure 4). The two planes formed by the two intramolecular chelates are antitwisted[43] by an angle of 38°. Similar trends have been reported for other mononuclear homoleptic Pd(II) complexes.[44] The two $Cr(CO)_3$ groups are in a syn relationship that entails an increased steric hindrance between the two adjacent chelates. This is revealed by the relatively short C13−C15 and C4−C18 interatomic distances of 3.297(6) and 3.435(6) Å, respectively. Furthermore, each 2-phenylpyridyl chelate presents a significant noncoplanarity, characterized, for instance, by a value of ca. 9° for the dihedral angle C7−C8−C9−C10.

Spectroscopic Properties of the Binuclear Complexes. The new complexes reported herein have been investigated by various spectroscopic and analytical methods and displayed satisfactory results as far as purity is concerned. We also attempted to extract information about seldom-documented electronic properties of the σ-bonded metallic fragments. The IR spectra of (η^6-arene)$Cr(CO)_3$ complexes offer a direct access to the electronic properties of a given arene substituent, which causes a shift of the carbonyl C−O bond vibration frequencies directly related to a variation of electron density at the arene ring. By calculating the approximate C−O bond force constant, one may approach the amplitude of either the electron-donating or -withdrawing effect of a given arene substituent.[45] An electron-donating group should induce a flow of electron density toward the Cr atom that induces an increase of the back-donation of the latter to the π^* orbital of the CO ligand and a decrease of both the C−O bond order and the corresponding bond force constant k_{CO}.

In Table 4, we have listed the IR data of the main dinuclear complexes reported herein together with the data of rare cases of similar Pd(II) and Hg(II) complexes reported in the literature. The constant k_{CO} and the approximated interaction constant between two cis CO ligands k_i have been calculated following the classical Cotton−Kraihanzel treatment.[46] Δk_{CO} characterizes the variation of the force constant upon replacement of a H atom by the metal-centered substituent: a negative value denotes an electron-donating effect. The electronic effects of the ligands surrounding the σ-bonded metal are readily transmitted to the $Cr(CO)_3$ moiety, as can be noted for complexes **5d**−**j**[16] (Chart 3) with a decrease of Δk_{CO} from the μ-chloro-bridged Pd(II) complexes to the monomers bearing di- or monophosphines (Table 4, entries 9−15). In complexes **1b**, **2b**, and **3b** the chelated −HgCl moiety results in almost no variation of k_{CO} relative to **1a**, **2a**, and **3a**, respectively, probably because of a chelation of the mercury atom by the intramolecular nitrogen Lewis base (Table 4, entries 1−3). Indeed, the values of Δk_{CO} related to the last three complexes are

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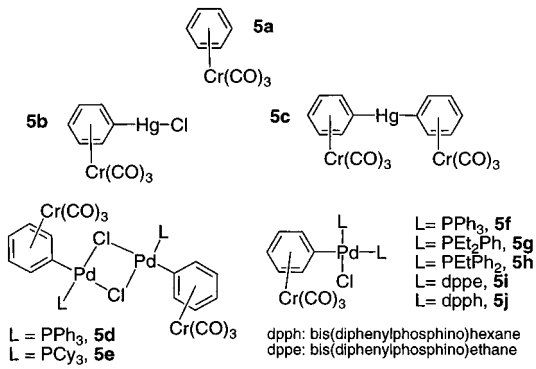
Table 4. IR Vibration Bands of Mercurated and Palladated (η^6-arene)Cr(CO)$_3$ Complexes: CO Bond Stretching Force Constants, k_{CO}, Interaction Constant between Two Adjacent CO Groups, k_i, and the Corresponding Value of $\Delta k_{CO} = k_M - k_H$

entry	Ar−H; A_1 and E bands (cm^{-1})	k_{CO}, k_i (mdyn Å^{-1})	Ar−M; A_1 and E bands (cm^{-1})	k_{CO}, k_i (mdyn Å^{-1})	Δk_{CO} (mdyn Å^{-1})
1	**1a**; 1970,1980	14.89, 0.39	**1b**; 1969, 1899	14.93, 0.36	0.04
2	**2a**; 1969, 1889	14.82, 0.41	**2b**; 1966, 1890	14.82, 0.39	0.00
3	**3a**; 1976, 1904	15.01, 0.37	**3b**; 1975, 1905	15.02, 0.36	0.01
4	**4a**; 1969, 1897	14.91, 0.37	**4b**; 1965, 1889	14.80, 0.39	−0.10
5			**1i**; 1960, 1889	14.78, 0.36	−0.11
6			**2e**; 1954, 1874	14.59, 0.41	−0.23
7	**5a**; 1971, 1874, 1860[a,b]	14.62, 0.53	**5b**; 1970, 1890[b]	14.85, 0.41	0.23
8			**5c**; 1970, 1850[b]	14.44, 0.62	−0.18
9			**5d**; 1947, 1867[b]	14.49, 0.41	−0.13
10			**5e**; 1953, 1871[b]	14.56, 0.42	−0.06
11			**5f**; 1947, 1867[b]	14.49, 0.41	−0.13
12			**5g**; 1945, 1849[b]	14.30, 0.49	−0.32
13			**5h**; 1940, 1850[b]	14.29, 0.45	−0.33
14			**5i**; 1940, 1841[b]	14.20, 0.50	−0.42
15			**5j**; 1950, 1860[b]	14.44, 0.46	−0.18

[a] See ref 47d. [b] KBr pellet.

Chart 3



much lower than the large positive effect computed for (η^6-C$_6$H$_5$-HgCl)Cr(CO)$_3$ (Table 4, entry 7), i.e., **5b**,[3] in which the apparently strong electron-withdrawing effect of −HgCl directly stems from the marked ionic character of the Hg−Cl bond and the attractive inductive effect of Cl. In the Ar$_2$Hg-type complex **5c**,[47] a large negative value for Δk_{CO} is obtained (Table 4, entry 8). For Pd(II) complexes **1i** and **2e** (Table 4, entries 5 and 6) and **5d**−**j** negative Δk_{CO} values suggest that the metal-centered unit behaves as an electron-donating group.

Mercury compounds have been increasingly studied by ^{199}Hg NMR spectroscopy, which is nowadays considered as a promising and valuable structural metallobioprobe.[48] With modern FT NMR spectrometers, ^{199}Hg solution NMR spectra of most mercury compounds can be obtained with satisfactory signal/noise ratios, provided that the solubility of the compound has been optimized in an appropriate solvent. The interest in ^{199}Hg NMR stems from the sensitivity of the nucleus to factors related to the chemical environment such as concentration, the nature of the solvent, and the basicity[49] of mercury's ligand(s). It is established that the

Table 5. List of ^{199}Hg Chemical Shifts for the Reported Ar−HgX and Ar$_2$Hg Complexes.

compd	solvent	spectrometer ref freq (MHz)	peak chem shift(s) (δ, ppm)
1b	C_3D_6O	89.574 16	−940
2b	C_3D_6O		−963
1c	$CDCl_3$		−683
2c, **2d**	C_3D_6O		−634, −638

^{199}Hg chemical shift shows some dependence on the amount of ionic character of Hg−X bonds. In our case, the solubility of the complexes was satisfactory at subambient temperatures in acetone as well as in chloroform. Table 5 lists the chemical shifts of the ^{199}Hg signals observed for chloromercuric complexes **1b** and **2b** and for the "symmetrized" complexes **1c**, **2c**, and **2d**. All the spectra were referenced against Ph_2Hg (δ −750 ppm[50]) in deuterated acetone and chloroform. Similarly to observations made for mononuclear mercury(II) complexes, ^{199}Hg signals for **1c** and **2c**,**d** were detected about 250−300 ppm downfield from those of **1b** and **2b**, respectively. These two groups of compounds produced ^{199}Hg signals at frequencies similar to those reported for 2-phenylpyridine chloromercuric and "symmetrized" Ar−Hg−Ar derivatives.

Conclusion

Herein, we have shown that the ortho mercuration of (η^6-arene)Cr(CO)$_3$ complexes bearing endogenous nitrogen ligands was possible, although a deeper study of the interaction of HgX_2-type species with ambident (η^6-arene)Cr(CO)$_3$ substrates is warranted. We have shown that these mercurated complexes have significant potential for further applications in metal-mediated organic as well as inorganic syntheses. In our future reports, these aspects will be especially addressed with planar asymmetric (η^6-arene)tricarbonylchromium complexes. We have further shown that transmetalation could readily open the route to new cyclopalladated complexes with interesting structural features and numerous possible applications in palladium-mediated syntheses and homogeneous catalysis.

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Experimental Section

All experiments were carried out under a dry atmosphere of argon with dry and degassed solvents. Starting (η^6-arene)-tricarbonylchromium complexes **1a**, **2a**, and **4a** were synthesized by applying published procedures.[19,20] Dichloro(η^3-allyl)-palladium(II) was purchased from Aldrich and used without preliminary purification. NMR spectra were acquired on Bruker DRX 500 (^{199}Hg, ^{13}C, and ^{1}H nuclei) and AC 300 (^{1}H nucleus) spectrometers at room temperature unless otherwise stated. Chemical shifts were reported in parts per million downfield of Me_4Si. IR spectra were measured on a Perkin-Elmer FT spectrometer. Mass spectra were performed at the Service of Mass Spectrometry of University Louis Pasteur. Elemental analyses (reported in percent mass) were performed at the Service d'Analyses of the "Institut de Chimie de Strasbourg" and at the analytical center of the "Institut Charles Sadron" in Strasbourg.

Experimental Procedure for the X-ray Diffraction Analysis of Compounds 1b, 1c, 1i, and 1j. Acquisition and processing parameters are displayed in Table 3. Reflections were collected on a KappaCCD diffractometer using Mo Kα graphite-monochromated radiation (λ = 0.710 73 Å). The structure was solved using direct methods and refined against $|F|$. Hydrogen atoms were introduced as fixed contributors. For all computations the Nonius OpenMoleN package was used.[51]

Synthesis of Complex 1b. A suspension of **1a** (3.00 g, 10.3 mmol) and $Hg(OAc)_2$ (4.90 g, 15.4 mmol) in EtOH (10 mL) was stirred at reflux during 4 h under argon. The resulting dark orange solution was cooled to room temperature and filtered through Celite. Upon addition of a saturated solution of $CaCl_2$ in EtOH to the filtrate a bright orange solid precipitated. The latter solid was filtered, washed with water, and dried under vacuum. Recrystallization of the yellow powder from a dry CH_2Cl_2/hexane mixture afforded **1b** (4.60 g, 85% yield). Anal. Calcd for $C_{14}H_8NO_3ClCrHg{\cdot}CH_2Cl_2$: C, 29.48; H, 1.65; N, 2.29. Found: C, 29.68; H, 1.60; N, 2.45. HRMS: calcd for $C_{14}H_8NO_3Cl^{52}Cr^{200}Hg$, 524.9281; found, 524.9299. IR (CH_2Cl_2): ν(CO) 1899, 1969 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.61 (d, ^3J = 4.3 Hz, 1H, Py), 7.86 (t, ^3J = 7.8 Hz, 1H, Py), 7.71 (d, ^3J = 8.0 Hz, 1H, Py), 7.43 (dd, ^3J = 4.8, 7.3 Hz, 1H, Py), 5.99 (d, ^3J = 6.2 Hz, 1H, ArCr), 5.60 (m, 2H, ArCr), 5.48 (t, ^3J = 6.1 Hz, 1H, ArCr). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 232.4 (CO), 153.1, 148.0, 138.4, 124.5, 120.0, 108.9, 105.5, 100.9, 93.1, 93.0, 90.6. MS (FAB+): *m/e* 527 [M]$^+$, 471 [M − 2CO]$^+$, 390 [M − Cr(CO)$_3$]$^+$, 292 [M − HgCl]$^+$.

Synthesis of Complex 2b. The reactants, conditions, and results were as follows: **2a** (580 mg, 2.14 mmol), $Hg(OAc)_2$ (1.02 g, 3.21 mmol), EtOH (10 mL); reflux for 3 h and saturated solution of $CaCl_2$ in EtOH; recrystallization with CH_2Cl_2/hexane; yellow complex **2b** (410 mg, 0.81 mmol, 38% yield). Anal. Calcd for $C_{12}H_{12}NO_3ClCrHg{\cdot}CH_2Cl_2$: C, 26.39; H, 2.36; N, 2.37. Found: C, 26.24; H, 2.32; N, 2.45. HRMS: calcd for $C_{12}H_{12}NO_3Cl^{52}Cr^{200}Hg$, 504.9594; found, 504.9605. IR (CH_2Cl_2): ν(CO) 1890, 1966 cm^{-1}. ^{1}H NMR (C_6D_6): δ 4.37 (m, 2H, ArCr), 4.27 (t, ^3J = 4.6 Hz, 2H, ArCr), 2.78 (d, ^2J = 14.9 Hz, 1H, CH_2), 2.18 (d, ^2J = 14.9 Hz, 1H, CH_2), 1.74 (s, 6H, $N(CH_3)_2$). ^{13}C{^{1}H} NMR (C_3D_6O): δ 235.1 (CO), 115.5, 103.3, 102.6, 96.9, 95.4, 95.1, 62.7, 44.9, 44.8. MS (FAB+): *m/e* 507 [M]$^+$, 451 [M − 2CO]$^+$, 423 [M − 3CO]$^+$, 370 [M − Cr(CO)$_3$]$^+$.

Preparation of 3a. A mixture of phenyl-2-oxazoline (4 g, 0.027 mol) and $Cr(CO)_6$ (6 g, 0.027 mol) was dissolved in *n*-Bu_2O (150 mL), and THF (10 mL) was added to the resulting mixture. The suspension was gently refluxed for 7 days. The resulting yellow solution was cooled to room temperature and filtered through Celite. The filtrate was evaporated under reduced pressure, the resulting oil redissolved in CH_2Cl_2, and silica gel added. After evaporation of the solvent under reduced pressure, the coated silica gel was loaded on the top of a SiO_2 (60 μm) column packed in *n*-hexane. Complex **3a** was eluted with pure CH_2Cl_2. The solvent was removed under vacuum and the bright yellow solid recrystallized from a CH_2Cl_2/hexane mixture (1.87 g, 24%). Anal. Calcd for $C_{12}H_9NO_4Cr$: C, 50.88; N, 4.95; H, 3.20. Found: C, 51.04; N, 5.07; H, 2.99. IR (CH_2Cl_2): ν(CO) 1976, 1904 cm^{-1}. ^{1}H NMR (C_6D_6): δ 5.75 (d, 2H, ^3J = 6.8 Hz, H_{ortho}), 4.40 (t, 1H, ^3J = 6.1 Hz, H_{para}), 4.31 (t, 2H, ^3J = 6.1 Hz, H_{meta}), 3.59 (*t**, 2H, J = 10 Hz, $H_{oxazoline}$), 3.43 (t*, 2H, J = 11 Hz, $H_{oxazoline}$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 231.6 (CO), 162.5, 128.4, 93.4, 92.7, 91.1, 90.5, 68.3, 54.9.

Synthesis of 3b. The reactants, conditions, and results were as follows: **3a** (550 mg, 1.96 mmol), $Hg(OAc)_2$ (940 mg, 2.95 mmol), EtOH (10 mL), and saturated solution of $CaCl_2$ in EtOH; reflux for 3 h; recrystallization with CH_2Cl_2/hexane; yellow complex **3b** (170 mg, 17% yield). Anal. Calcd for $C_{12}H_8NO_4ClCrHg$: C, 27.74; H, 1.54; N, 2.69. Found: C, 27.80; H, 1.83; N, 2.57. HRMS (FAB$^+$): calcd for $C_{12}H_8NO_4Cl^{52}Cr^{200}Hg$, 516.9230; found, 516.9246. IR (CH_2Cl_2): ν(CO) 1905, 1975 cm^{-1}. ^{1}H NMR (C_6D_6): δ 5.38 (d, ^3J = 6.3 Hz, 1H, ArCr), 4.42 (t, ^3J = 6.3 Hz, 1H, ArCr), 4.25 (t, ^3J = 6.3 Hz, 1H, ArCr), 3.98 (d, ^3J = 6.1 Hz, 1H, ArCr), 3.40 (m, 2H, CH_2), 3.05 (m, 2H, CH_2). ^{13}C{^{1}H} NMR (C_3D_6O): δ 233.8 (CO), 168.0, 114.9, 102.7, 101.7, 97.3, 95.4, 93.6, 70.5, 54.5. MS (FAB$^+$): *m/e* 519 [M]$^+$, 462 [M − 2CO]$^+$, 384 [M − Cr(CO)$_3$]$^+$.

Synthesis of 4b. The reactants, conditions, and results were as follows: **4a** (1.00 g, 3.51 mmol), $Hg(OAc)_2$ (1.68 g, 5.26 mmol), EtOH (10 mL); reflux for 3 h and saturated solution of $CaCl_2$ in EtOH; recrystallization with CH_2Cl_2/hexane; yellow complex **4b** (860 mg, 47% yield). $[\alpha]_D(CH_2Cl_2, 298\ K) = +64.5°$ ($c = 1.7 \times 10^{-3}$ M). Anal. Calcd for $C_{13}H_{14}NO_3ClCrHg{\cdot}{}^1/_2CH_2Cl_2$: C, 28.81; H, 2.69; N, 2.49. Found: C, 29.00; H, 2.90; N, 2.38. HRMS (FAB+): calcd for $C_{13}H_{14}NO_3Cl^{52}Cr^{199}Hg$, 517.9750; found, 517.9745. IR (CH_2Cl_2): ν(CO) 1889, 1965 cm^{-1}. ^{1}H NMR (C_6D_6): δ 4.45 (m, 4H, ArCr), 3.02 (q, ^3J = 6.6 Hz, 1H, CH), 1.71 (s, 6H, $N(Me)_2$), 0.51 (d, ^3J = 6.8 Hz, 3H, CH_3). ^{1}H NMR ($CDCl_3$): δ 5.50 (d, ^3J = 6.1 Hz, 1H, ArCr), 5.45 (t, ^3J = 6.1 Hz, 1H, ArCr), 5.37 (d, ^3J = 6.4 Hz, 1H, ArCr), 5.30 (t, ^3J = 5.9 Hz, 1H, ArCr), 3.54 (q, ^3J = 6.2 Hz, 1H, CH), 2.30 (s, 6H, $N(Me)_2$), 1.25 (d, ^3J = 6.6 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 233.0 (CO), 116.8, 113.6, 100.5, 93.0, 92.7, 92.4, 62.0, 40.0, 9.9. MS (FAB+): *m/e* 521 [M]$^+$, 465 [M − 2CO]$^+$, 437 [M − 3CO]$^+$, 384 [M − Cr(CO)$_3$]$^+$, 285.2 [M − HgCl]$^+$.

Symmetrization of 1b into 1c and 1d. Complex **1b** (1.60 g, 3.04 mmol) and tetramethylammonium chloride (400 mg, 3.65 mmol) were dissolved in dry acetone (10 mL). The mixture was stirred at reflux over 15 h. The solution was cooled to room temperature and filtered through Celite. The solvent was evaporated under reduced pressure. The resulting residue was recrystallized from dry CH_2Cl_2/hexane, affording a 2.33:1 mixture of **1c** and **1d,** respectively (1.06 g, 90% conversion). Mixture of **1c** and **1d**: Anal. Calcd for $C_{28}H_{16}N_2O_6Cr_2Hg{\cdot}{}^1/_2CH_2Cl_2$: C, 41.57; H, 2.08; N, 3.40. Found: C, 41.44; H, 2.34; N, 3.38. HRMS: calcd for $C_{28}H_{17}N_2O_6{}^{52}Cr_2{}^{200}Hg$ (MH^+), 779.9579; found, 779.9567. IR (CH_2Cl_2): ν(CO) 1883, 1960 cm^{-1}. Complex **1c**: ^{1}H NMR (C_6D_6) δ 8.20 (d, ^3J = 4.9 Hz, 1H, Py), 6.93 (m, 2H, Py), 6.45 (dd, ^3J = 4.9, ^4J = 1.2 Hz, 1H, Py), 5.22 (dd, ^3J = 6.8, ^4J = 1.0 Hz, 1H, ArCr), 5.11 (dd, ^3J = 7.6, ^4J = 1.4 Hz, 1H, ArCr), 4.78 (m, 2H, ArCr); ^{13}C{^{1}H} NMR ($CDCl_3$, 288 K) δ 234.3, 155.7, 148.4, 137.4, 125.5, 123.6, 120.6, 111.0, 102.3, 94.5, 94.2, 93.1. Complex **1d**: ^{1}H NMR (C_6D_6) δ 8.23 (d, 1H, Py), 6.99 (m, 2H, Py), 6.52 (dd, ^3J = 4.9 ^4J = 1.4 Hz, 1H, Py), 5.28 (m, 1H, ArCr), 5.07 (dd, ^3J = 4.6 ^4J = 2.7 Hz, 1H, ArCr), 4.78 (m, 2H, ArCr); ^{13}C{^{1}H} NMR ($CDCl_3$, 288 K) δ 234.1, 156.2, 148.6, 137.6, 125.4, 123.6, 120.8, 110.5, 102.4, 94.8, 93.8, 92.7; MS (FAB$^+$) *m/e* 783 [M + H]$^+$, 698 [M − 3CO]$^+$, 666, 647 [M − Cr(CO)$_3$]$^+$, 596, 496, 412, 360.

Symmetrization of 2b into 2c and 2d. The reactants, conditions, and results were as follows: **2b** (450 mg, 0.89 mmol), Me_4NCl (120 mg, 1.09 mmol), acetone (10 mL), reflux for 3 h; recrystallization with CH_2Cl_2/hexane; 1:0.45 mixture of **2c** and **2d** (0.22 g, 0.29 mmol, 67% yield). Mixture of **2c**

(51) Fair, C. K. In *MolEN: An Interactive Intelligent System for Crystal Structure Analysis*; Nonius: Delft, The Netherlands, 1990.

and **2d**: Anal. Calcd for $C_{24}H_{24}N_2O_6Cr_2Hg$: C, 38.90; H, 3.26; N, 3.78. Found: C, 39.06; H, 3.12; N, 3.66. HRMS (FAB+): calcd for $C_{24}H_{24}N_2O_6Cr_2Hg$, 740.0127; found, 740.0161. IR (CH_2Cl_2): ν(CO) 1879, 1958 cm^{-1}. MS (FAB+): 741 $[M]^+$, 658 $[M - 3CO]^+$, 605 $[M - Cr(CO)_3]^+$. Complex **2c**: ^1H NMR (C_6D_6, 300 MHz) δ 4.93 (d, $^3J = 6.1$ Hz, 1H, ArCr), 4.68 (dd, $^3J = 6.5$, $^4J = 1.0$ Hz, 1H, ArCr), 4.54 (dd, $^3J = 5.8$ Hz, 2H, ArCr), 3.30 (d, $^2J = 13.6$ Hz, 1H, CH_2), 2.24 (dd, $^2J = 13.7$ Hz, 1H, CH_2), 1.95 (s, 6H, NMe_2); ^1H NMR (C_3D_6O, 300 MHz) δ 5.78 (dd, $^3J = 5.5$, $^4J = 1.2$ Hz, 1H, ArCr), 5.70 (dd, $^3J = 6.3$, $^4J = 1.2$ Hz, 1H, ArCr), 5.59 (dd, $^3J = 6.3$ Hz, 1H, ArCr), 5.51 (dd, $^3J = 6.1$, $^4J = 1.2$ Hz, 1H, ArCr), 3.64 (d, $^2J = 13.4$ Hz, 1H, CH_2), 2.96 (d, $^2J = 13.6$ Hz, 1H, CH_2), 2.38 (s, 6H, NMe_2); ^{13}C NMR (C_3D_6O) δ 236.0, 129.9, 118.5, 104.9, 97.3, 95.8, 94.8, 65.3, 45.2. Complex **2d**: ^1H NMR (C_6D_6) δ 4.90 (d, $^3J = 7.3$ Hz, 1H, ArCr), 4.68 (dd, $^3J = 6.5$, $^4J = 1.0$ Hz, 1H, ArCr), 4.48 (m, 2H, ArCr), 3.40 (d, $^2J = 13.4$ Hz, 1H, CH_2), 2.15 (dd, $^2J = 14.0$ Hz, 1H, CH_2), 2.09 (s, 6H, NMe_2); ^1H NMR (C_3D_6O) δ 5.78 (dd, $^3J = 5.5$, $^4J = 1.2$ Hz, 1H, ArCr), 5.65 (dd, $^3J = 6.8$, $^4J = 1.2$ Hz, 1H, ArCr), 5.59 (dd, $^3J = 6.3$ Hz, 1H, ArCr), 5.51 (dd, $^3J = 6.1$, $^4J = 1.2$ Hz, 1H, ArCr), 3.62 (d, $^2J = 13.4$ Hz, 1H, CH_2), 2.99 (d, $^2J = 13.4$ Hz, 1H, CH_2), 2.42 (s, 6H, NMe_2); $^{13}C\{^1H\}$ NMR (C_3D_6O) δ 235.9, 130.1, 118.4, 104.7, 97.4, 95.5, 94.9, 65.3, 45.3.

Symmetrization of 4b into 4c. Complex **4b** (400 mg, 077 mmol), Me_4NCl (100 mg, 0.92 mmol), acetone (10 mL), reflux for 5 h; recrystallization from CH_2Cl_2/hexane: complex **4c** (150 mg, 50% yield). $[\alpha]_D(CH_2Cl_2, 298\ K)$: +114.8° ($c = 1.7 \times 10^{-5}$ M). Anal. Calcd for $C_{26}H_{28}N_2O_6Cr_2Hg$: C, 40.52; H, 3.64; N, 3.64. Found: C, 40.44; H, 3.83; N, 3.41. HRMS (FAB+): calcd for $C_{26}H_{29}N_2O_6{}^{52}Cr_2{}^{200}Hg$ (MH^+), 769.0519; found, 769.0498. IR (CH_2Cl_2): ν(CO) 1959, 1877 cm^{-1}. ^1H NMR (C_6D_6): δ 4.91 (d, $^3J = 5.6$ Hz, 1H, ArCr), 4.67 (m, 2H, ArCr), 4.56 (t, 1H, ArCr), 3.41 (q, $^3J = 6.4$ Hz, 1H, CH), 2.03 (s, 6H, NMe_2), 0.75 (d, $^3J = 6.8$ Hz, 3H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 234.6, 129.7, 120.1, 102.7, 93.4, 93.3, 93.2, 63.0, 40.3, 8.2. MS (FAB+): *m/e* 769 $[M]^+$, 686 $[M - 3CO]^+$, 633 $[M - Cr(CO)_3]^+$.

Formation of 4d. Complex **4c** (200 mg, 0.26 mmol) was dissolved in dry THF (10 mL) and reacted with a solution of *n*-BuLi in hexane (1.6 M, 0.35 mL, 0.57 mmol) at −78 °C for 15 min. The reaction mixture was then warmed to −60 °C and stirred for 4.5 h. An excess of MeI (0.53 mL, 0.85 mmol) was added to the brown-orange solution and the resulting mixture warmed slowly to room temperature. Absolute methanol and SiO_2 were added to the solution, and the solvents were removed under reduced pressure. The coated SiO_2 was loaded on the top of a silica gel column packed in hexane. After elution with a mixture of CH_2Cl_2/ and acetone (3:1) and subsequent evaporation of the solvents under reduced pressure, complex **4d** was recovered as a canary yellow powder (45 mg, 29% yield). Spectrosopic data obtained for **4d** were identical with those reported in the literature.[12m,p] $[\alpha]_D(CHCl_3, 293\ K) = -51.4°$ ($c = 1.03$ g/100 mL). IR ($CHCl_3$): ν(CO) 1965, 1889 cm^{-1}. ^1H NMR (C_6D_6): δ 4.81 (d, 1H, H_{Ar}), 4.54 (t, 1H, H_{Ar}), 4.33 (m, 2H, H_{Ar}), 3.35 (q, 1H, C*H*-Me), 1.88 (s, 3H, C_{Ar}−Me), 1.79 (s, 6H, N*Me*$_2$), 0.89 (d, 3H, CH−*Me*).

Synthesis of 1i. A solution of $PdCl_2(MeCN)_2$ (110 mg, 0.43 mmol) in dry acetone (10 mL) was added dropwise to a solution of a mixture of **1c** and **1d** (340 mg, 0.43 mmol) in acetone (40 mL) at −15 °C. The resulting mixture was stirred and slowly warmed to room temperature within 4 h, the solution was filtered over Celite, and the solvent was removed under reduced pressure. The orange residue was separated by flash chromatography on silica gel. Complex **1b** was first eluted with acetone/hexane (20/80), followed by a mixture of dimers **1e**−**h** (acetone-hexane 50:50). The monomer **1i** was obtained by addition of excess pyridine to the latter raw fraction containing the dimers. The resulting solution was filtered over Celite and the solvent removed under reduced pressure. Flash chromatography over silica gel (acetone/hexane, 50:50) afforded the orange complex **1i** (0.13 g, 0.25 mmol, 58% yield). Complex **1i**: Anal. Calcd for $C_{19}H_{13}N_2O_3CrPdCl{\cdot}CH_2Cl_2$: C, 40.30; H, 2.54; N, 4.70. Found: C, 40.97; H, 2.67; N, 4.65. HRMS (FAB+): calcd for $C_{19}H_{13}N_2O_3Cl^{52}Cr^{106}Pd$, 509.9054; found, 509.9065. IR (CH_2Cl_2): ν(CO) 1960, 1889 cm^{-1}. ^1H NMR (C_3D_6O): δ 9.45 (d, $^3J = 5.8$ Hz, 1H, Py), 9.01 (d, $^3J = 6.3$ Hz, 2H, Py-Pd), 8.14 (m, 2H, Py), 7.91 (d, $^3J = 8.3$ Hz, 1H, Py), 7.74 (dd, $^3J = 6.6$ Hz, 2H, Py-Pd), 7.47 (t, $^3J = 6.6$ Hz, 1H, Py-Pd), 6.38 (d, $^3J = 6.1$ Hz, 1H, ArCr), 5.54 (m, 2H, ArCr), 4.48 (d, $^3J = 5.9$ Hz, 1H, ArCr). $^{13}C\{^1H\}$ NMR (C_3D_6O): δ 234.8, 164.3, 153.6, 152.5, 140.7, 139.8, 126.9, 124.3, 121.5, 119.7, 111.5, 96.5, 93.0, 91.2. MS (FAB+): *m/e* 512 $[M]^+$, 428 $[M - 3CO]^+$, 393 $[M - Cl - 3CO]^+$.

Alternative Method for the Synthesis of 1i. The procedure for this reaction was similar to that described with $(MeCN)_2PdCl_2$. The conditions were as follows: $[(\eta^3\text{-allyl})PdCl]_2$ (140 mg, 0.38 mmol) solution in acetone (7 mL), compound **1b** (400 mg, 0.76 mmol) in acetone (30 mL); the reaction medium was warmed during 6 h from −15 °C to room temperature and excess pyridine was added; chromatography over SiO_2 with an acetone/hexane mixture (50:50) afforded the orange complex **1i** (210 mg, 54% yield).

Synthesis of 2e. A solution of $PdCl_2(MeCN)_2$ (0.08 g, 0.30 mmol) in dry acetone (10 mL) was added dropwise to a solution of a mixture of **2c** and **2d** (0.22 g, 0.30 mmol) in acetone (40 mL) at −15 °C. The resulting mixture was stirred and slowly warmed to room temperature over 7 h. Excess pyridine was added dropwise to the medium, the resulting solution was stirred for additional 15 min and filtered over Celite, and the solvent was removed under reduced pressure. The product was purified by flash chromatography over silica gel. The starting compound was first eluted with pure CH_2Cl_2, followed by the orange product **2e** (0.05 g, 0.10 mmol, 33%), which was eluted with an acetone/hexane (50:50) mixture. Anal. Calcd for $C_{17}H_{17}N_2O_3ClCrPd$: C, 41.55; H, 3.46; N, 5.70. Found: C, 41.49; H, 3.83; N, 5.24. HRMS (FAB+): calcd for $C_{17}H_{17}N_2O_3Cl^{52}Cr^{106}Pd$, 489.9367; found, 489.9372. IR (CH_2Cl_2): ν(CO) 1874, 1954 cm^{-1}. ^1H NMR (C_6D_6): δ 8.73 (broad, 2H, Py), 6.61 (t, 1H, Py), 6.35 (broad, 2H, Py), 4.63 (broad, 2H, ArCr), 4.24 (dd, $^3J = 5.7$ Hz, 1H, ArCr), 3.86 (d, $^3J = 6.2$ Hz, 1H, ArCr), 3.11 (d, $^2J = 15.0$ Hz, 1H, CH_2), 2.84 (s, 3H, NMe_2), 2.65 (d, $^2J = 15.0$ Hz, 1H, CH_2), 2.45 (s, 3H, NMe_2). ^1H NMR ($CDCl_3$): δ 8.93 (d, $^3J = 5.1$ Hz, 2H, Py), 7.86 (t, $^3J = 7.8$ Hz, 1H, Py), 7.46 (t, 2H, Py), 5.22 (d, $^3J = 6.4$ Hz, 1H, ArCr), 5.14 (t, $^3J = 6.2$ Hz, 1H, ArCr), 4.90 (t, $^3J = 6.3$ Hz, 1H, ArCr), 4.05 (d, $^3J = 6.3$ Hz, 1H, ArCr), 3.88 (d, $^2J = 14.9$ Hz, 1H, CH_2), 3.69 (d, $^2J = 14.9$ Hz, 1H, CH_2), 3.14 (s, 3H, $N(Me)_2$), 2.94 (s, 3H, $N(Me)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 234.4 (CO), 152.7, 138.4, 125.7, 118.5, 116.0, 96.7, 91.6, 90.9, 88.4, 71.7, 53.0, 52.8. MS (FAB+): *m/e* 492 $[M]^+$, 455 $[M - Cl]^+$, 406 $[M - 3CO]^+$, 319 $[M - Cl - Cr(CO)_3]^+$.

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Supporting Information Available: Listings of crystallographic and structural data for compounds **1b**, **1c**, **1i**, and **1j**. This material is available free of charge via the Internet at http://pubs.acs.org.

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