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Symmetrization of Phenylmercuric Hydroxides by the Action of Nickel(II) and Cobalt(II) Acetylacetonates. Isolation and Structural Characterization of an Intermediate in This Reaction

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The complex adducts [M(acac)$_2$(PhHgOHgPh)]$_2$ (M = Co, Ni) have been obtained by incorporation of PhHgOH into the coordination sphere of M(acac)$_2$ at ambient temperature. The X-ray crystal structure of [Ni(acac)$_2$(PhHgOHgPh)(Et$_2$O)]$_2$ (**1c**) reveals a dimeric nickel complex coordinated by the acetylacetonate oxygen and the bridging oxygen of bis(phenylmercuric) oxide. Refluxing a THF solution of compound **1c** gave diphenylmercury, HgO, and Ni(acac)$_2$(THF)$_2$. With PhHgOH or PhHgSH the symmetrization reactions also occurred when catalytic amounts of Ni(acac)$_2$ were used. In contrast, triphenyltin derivatives (hydroxide, acetate, oxide) on treatment with M(acac)$_2$ in aqueous THF gave the stable complexes [M(acac)$_2$(Ph$_3$SnOH)]$_2$ (M = Co, Ni). The structure of [Ni(acac)$_2$(Ph$_3$SnOH)]$_2$ (**2**) was also determined by X-ray crystallography.

Introduction

Metal(II) acetylacetonates M(acac)$_2$ (M = cobalt, nickel) form a series of adducts with alcohols, ethers, and ketones.[1] The ketone and ether adducts have gained attention as intermediates in the cross-coupling of Grignard reagents with acyl chlorides[2] and silyl enol ethers.[3] Furthermore, these metal(II) acetylacetonates have been used as catalysts in the formation of ethers from alcohols and alkyl halides.[4] The corresponding alcohol and ether adducts should be intermediates of that catalytic process. With regard to the catalytic ether formation, we are examining the chemistry of organomercuric and triorganotin hydroxides and oxides when they have been incorporated into the coordination sphere of nickel(II) and cobalt(II) acetylacetonates. Furthermore, recent studies on the detoxification of organomercurials in enzymatic processes[5] have stimulated renewed interest in the coordination chemistry of organomercury compounds.[6] Herein is reported the synthesis of bis(phenylmercuric) oxide adducts [M(acac)$_2$(PhHgOHgPh)]$_2$ (**1**) starting from phenylmercuric hydroxide or the corresponding halides. Structural details of the mercuric oxide bridged dimer [Ni(acac)$_2$(PhHgOHgPh)(OEt$_2$)]$_2$ (**1c**) are given. Refluxing of **1** in tetrahydrofuran or toluene afforded a symmetrization of PhHgOHgPh into Ph$_2$Hg and HgO. With ArHgOH or PhHgSH as the starting material, a catalytic variant of this symmetrization is possible. These reactions represent a valuable catalytic version of the known symmetrization reactions of RHgX[7] induced by stoichiometric amounts of Lewis bases such as phosphines[8] and amines.[9] In this paper we also describe the synthesis

Scheme 1

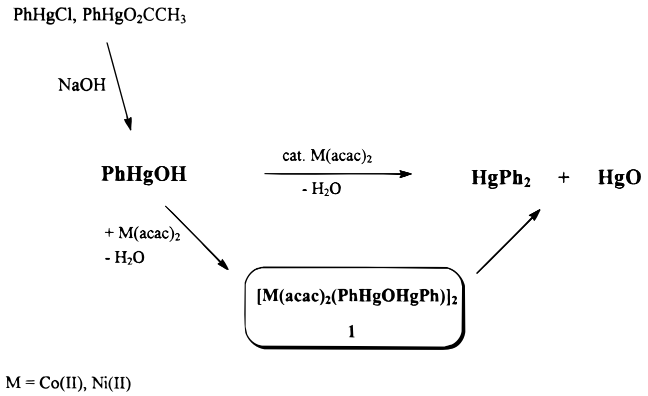

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Table 1. Crystallographic Data for Complexes 1c and 2

	1c	2
complex	$[Ni(acac)_2(PhHgOHgPh)(Et_2O)]_2$	$[Ni(acac)_2(Ph_3SnOH)]_2$
formula	$C_{52}H_{68}O_{12}Ni_2Hg_4$	$C_{56}H_{60}O_{10}Ni_2Sn_2$
M_r	1804.84	1247.84
cryst syst	tetragonal	triclinic
space group	$I4_1/acd$	$P\bar{1}$
T (K)	293	293
cryst size (mm)	0.3 × 0.25 × 0.5	0.4 × 0.4 × 0.4
a (Å)	18.953(2)	12.8551(3)
b (Å)	18.953(2)	12.8667(2)
c (Å)	33.173(4)	10.0971(6)
α (deg)	90	71.536(1)
β (deg)	90	73.684(1)
γ (deg)	90	100.576(3)
V (Å^3)	11916.1(1)	1450.6(1)
Z	8	1
F(000)	6656	632
D_{calc} (g cm^{-3})	2.012	1.428
μ(Ag Kα) (cm^{-1})	59.75	8.17
θ limit (deg)	3.08−19.2	3.05−18.00
scan mode	$\omega-2\theta$	$\omega-2\theta$
no. of rflns measd	18458	5390
no. of indep rflns	2453	4060
no. of obsd rflns $F_o^2 > 2\sigma(F_o^2)$	1639	3201
no. of params	154	318
GOF	1.005	1.024
R1	0.0300	0.0348
wR2	0.0608	0.0822

and molecular structure of the O(acac)-bridged dimer $[Ni(acac)_2(Ph_3SnOH)]_2$ (**2**), which was synthesized in the course of this study.

Results and Discussion

Syntheses, Molecular Structure, and Symmetrization Reaction of Bis(phenylmercuric) Oxide Coordinated to M(acac)$_2$. The reaction of 2 equiv of PhHgOH with M(acac)$_2$ (M = Co, Ni) at ambient temperature afforded the hexametallic complexes $[M(acac)_2(PhHgOHgPh)]_2$ (**1a**, M = Co; **1b**, M = Ni), respectively (Scheme 1). Depending on the solvent used, adducts of the type $[M(acac)_2(PhHgOHgPh)(solvent)]_2$ (solvent = THF, diethyl ether, acetone, DMF) were obtained. Furthermore, the complexes also were prepared in a one-pot procedure in generally good (67%) yield by hydrolysis of phenylmercuric chloride or acetate, respectively, followed by treatment with M(acac)$_2$. Two principal points reflected the particular stability of the complex compounds **1a** and **1b**: First, bis(phenylmercuric) oxide (PhHgOHgPh) was formed in the presence of M(acac)$_2$ at ambient temperature. In contrast, the synthesis of PhHgOHgPh in the absence of complexing agents required elevated temperature (100 °C) and reduced pressure (0.3 Torr).[10] Second, PhHgOHgPh is capable of displacing strongly coordinated ligands such as pyridine from their M(acac)$_2$ complexes to form adducts of the type **1**. To elucidate the molecular structure of the new paramagnetic phenylmercuric oxide/M(acac)$_2$ adducts, an X-ray structure determination of $[Ni(acac)_2(PhHgOHgPh)(Et_2O)]_2$ (**1c**) was carried out (Table 1). The single-crystal X-ray diffraction study established the hexametallic structure of a coordination dimer; a drawing of **1c** can be found in Figure 1. Because of the crystallographic $I\,4_1/acd$ symmetry, with two 2-fold axes through the Ni_2O_2 centroid and one 4-fold screw axis, only the bond distances and angles in one-fourth of the molecule are listed in Table 2. Due to this symmetry in **1c** there is a planar Ni_2O_2 core (internal angles ca. 82.0(3) and 98.0(3)°; Ni−Ni distance 3.16 Å). Surprisingly, the electron-deficient oxygen atoms of PhHgOHgPh act as bridging atoms between two *cis*-Ni(acac)$_2$ fragments.

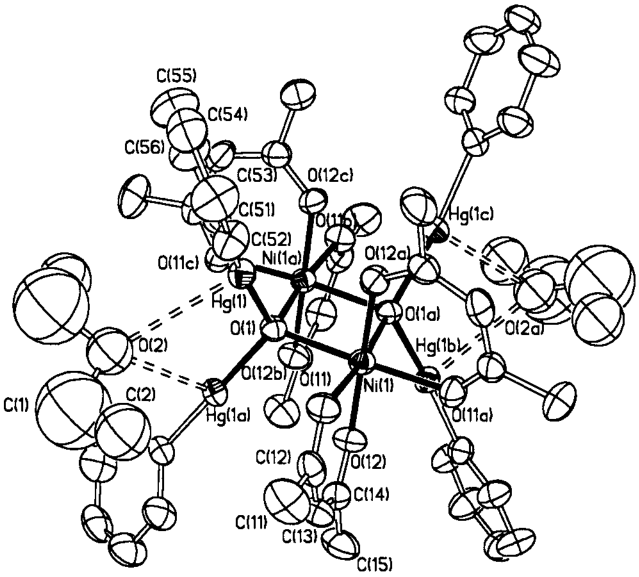

Figure 1. Molecular structure of complex **1c**. Thermal ellipsoids represent 30% probability contours.

Generally, the bridging function in metal acetylacetonates requires an electron-rich oxygen atom. One example for bridging by an oxygen atom of an additional ligand is found in $[Co(hfac)_2(NITEt)]_2$ (hfac = hexafluoroacetylacetonate, NITEt = 4,4,5,5-pentamethyl-2-ethyl-4,5-dihydro-1*H*-imidazolyl-1-oxy 3-oxide).[11] In electron-deficient O-donor ligands the bridging function is

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Table 2. Selected Bond Distances and Angles for the Complexes $[Ni(acac)_2(PhHgOHgPh)(Et_2O)]_2$ (1c) and $[Ni(acac)_2(Ph_3SnOH)]_2$ (2)

1c		2	
	Bond Lengths (Å)		
Ni(1)−O(1)	2.096(4)	Ni(1)−O(11)	2.044(3)
Ni(1)−O(11)	2.025(5)	Ni(1)−O(11a)	2.109(3)
Ni(1)−O(12)	2.010(5)	Ni(1)−O(12)	2.016(3)
Hg(1)−O(1)	2.041(3)	Ni(1)−O(21)	1.988(3)
Hg(1)−C(51)	2.042(8)	Ni(1)−O(22)	2.019(3)
Hg(1)−O(11)	3.228(6)	Ni(1)−O(30)	2.062(3)
Hg(1)−O(12a)	2.730(5)	O(22)−O(30a)	2.912(3)
Hg(1)−O(12c)	3.097(5)	Sn(1)−O(30)	1.983(3)
Hg(1)−O(2)	3.159(14)	Sn(1)−C(31)	2.128(4)
		Sn(1)−C(41)	2.121(5)
		Sn(1)−C(51)	2.194(9)
	Bond Angles (deg)		
O(1)−Ni(1)−O(1a)	82.1(3)	O(11)−Ni(1)−O(11a)	80.1(1)
O(1)−Ni(1)−O(11)	91.5(2)	O(11a)−Ni(1)−O(21)	103.0(1)
O(11)−Ni(1)−O(11a)	94.8(3)	O(12)−Ni(1)−O(21)	86.8(1)
O(11)−Ni(1)−O(12)	90.9(2)	O(21)−Ni(1)−O(22)	92.3(1)
O(11)−Ni(1)−O(12a)	88.5(2)	O(11a)−Ni(1)−O(30)	83.6(1)
Ni(1)−O(1)−Ni(1a)	97.9(3)	O(12)−Ni(1)−O(22)	97.1(1)
O(1)−Hg(1)−C(51)	175.0(2)	Ni(1)−O(11)−Ni(1a)	99.9(1)
Hg(1)−O(1)−Hg(1a)	119.4(3)	Ni(1)−O(30)−Sn(1)	131.7(2)
O(1)−Hg(1)−O(2)	86.2(3)	C(31)−Sn(1)−O(30)	110.2(2)
O(1)−Hg(1)−O(12a)	73.7(2)	C(51)−Sn(1)−O(30)	95.7(3)
O(1)−Hg(1)−O(12c)	65.2(2)	C(41)−Sn(1)−O(30)	108.0(3)
O(1)−Hg(1)−O(11)	63.6(3)		
C(51)−Hg(1)−O11)	112.7(2)		
C(51)−Hg(1)−O(12a)	101.5(2)		
C(51)−Hg(1)−O(12c)	114.5(3)		

undertaken by the more electron-rich atoms of the acac ligands, e.g., in the dimeric complexes $[Co(acac)_2(H_2O)]_2$ and $[Ni(acac)_2(piperidine)]_2$.[12] The bridging mode in **1c** is favored by an extension of the coordination number on mercury, a common phenomenon in the inorganic chemistry of mercury(II) compounds.[13] Using the maximum sum of van der Waals radii of oxygen (1.50 Å) and mercury (1.73 Å) for a bonding interaction[14] between oxygen and mercury, other weak intramolecular Hg−O(acac) interactions exist in **1c** with long Hg−O distances (Hg(1)−O(12a) = 2.730(5) Å, Hg(1)−O(12c) = 3.097(5) Å, Hg(1)−O(11) = 3.228(6) Å). With the additional secondary bonding between mercury and the oxygen atom of the ether, the mercury(II) atom has a effective coordination number of 5 or 6, resulting in a strongly distorted pentagonal or octahedral geometry around mercury(II). Similar complexes having secondary bonding interactions have been reported, e.g., 3.08(2) Å for the Hg−O distance of $[Hg(SC_5H_9NH(CH_3))_2][ClO_4]_2$[15] and 2.722(6), 2.826(6), and 3.189(6) Å for bis[2,6-bis(pivaloylamino)benzenethiolato]mercury.[16]

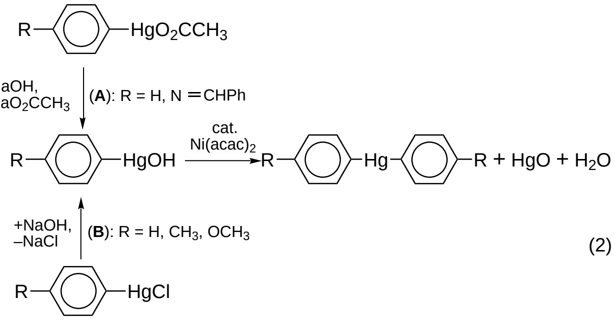
The ether oxygen atoms in **1c** interact simultaneously and symmetrically with both mercury atoms, but the length of the dative Hg−O bonds (3.16 Å) is very close to the sum of the van der Waals radii,[17] in contrast to the doubly coordinated carbonyl compounds by bidentate Lewis acids derived from 1,2-phenylenedimercury (2.68−2.77 Å).[18] Consequently, the solvent molecules are not strongly held at ambient temperature. The solvent-free complexes **1b** were obtained in pure form from **1c** in vacuo at 40 °C. The mercury(II) atoms in **1a** or **1b** exhibit a [2 + 3] coordination.[19]

To eliminate the coordinated PhHgOHgPh, THF and toluene solutions of the complexes **1** were heated at reflux or sublimation of the complexes was attempted. Instead of the expected release of PhHgOHgPh, the major products were diphenylmercury and mercuric oxide. This reaction can be explained in terms of a metal-assisted symmetrization of PhHgOHgPh (Scheme 1). $HgPh_2$ was isolated after flash chromatography in high (85%) yield. Treatment of phenylmercuric hydroxide with catalytic amounts of $M(acac)_2$ in refluxing THF or toluene also resulted in symmetrization to give $HgPh_2$. The catalytic symmetrization of phenylmercuric hydroxide with $M(acac)_2$ represents a far superior alternative to the symmetrization of phenylmercuric halides with stoichiometric amounts of phosphines[8] or amines[9] via formation of stable HgX_2 adducts according to eq 1.

$$2PhHgX + nL \rightarrow HgPh_2 + HgX_2L_n \qquad (1)$$

L = phosphines ($n = 2$), ammonia,
amines ($n = 2$), 2,2′-bipyridine,
bidentate phosphines ($n = 1$)[7−9]

Similar chemistry was observed with other arylmercuric hydroxides such as p-CH_3O-C_6H_4HgOH and p-CH_3-C_6H_4HgOH or the Schiff base p-Ph-CH=NC_6H_4HgOH prepared from the corresponding halides or acetates as shown in eq 2. The catalytic symmetrization provided the diarylmercury compound.



(2)

Phenylmercuric mercaptan (PhHgSH) also was symmetrized in the presence of a catalytic amount of Ni(acac)₂ according to eq 3. In this case, the reaction already proceeded at room temperature and an inter-

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(17) An analogous structure has been obtained with THF ligands instead of ether and Co(II) instead of Ni(II). $[Co(acac)_2(PhHgOHgPh)(THF)]_2$ ($C_{44}H_{44}O_{10}Co_2Hg_4$): M_r = 1801.26, monoclinic, $P2_1/c$, a = 10.466(1) Å, b = 22.390(2) Å, c = 12.715(1) Å, β = 103.623(6)°, V = 2895.6(4) Å^3, Z = 2, D_{calc} = 2.066 gcm^{-3}, λ(Ag Kα) = 0.560 142 Å, μ = 61.03 cm^{-1}, T = 293 K, R1 = 0.0358 for 2549 unique observed reflections with $F_o^2 > 2\sigma(F_o^2)$ and 323 parameters. Stoll, M.; Wolski, A. C.; Döring, M. Unpublished results.

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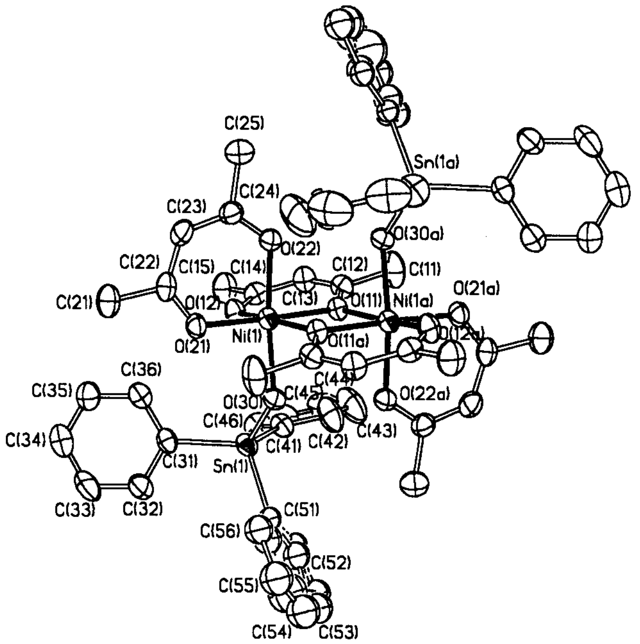
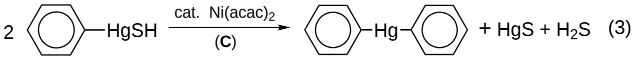


Figure 2. Molecular structure of complex **2**. Thermal ellipsoids correspond to 30% probability.

mediate bis(phenylmercuric) sulfide or a complex, analogous to **1**, was not isolable.



(3)

Syntheses and Molecular Structure of the Triphenyltin Hydroxide Adduct of Ni(acac)$_2$. When triphenyltin hydroxide was used instead of PhHgOH, formation of a comparable bis(triphenyltin) oxide complex was not observed. In contrast, a dimeric adduct of type [Ni(acac)$_2$(Ph$_3$SnOH)]$_2$ **2** was obtained. This complex also was formed by hydrolysis of triphenyltin acetate and bis(triphenyltin) oxide in the presence of a stoichiometric amount of Ni(acac)$_2$ according to eqs 4 and 5.

$$\mathrm{Ph_3SnOSnPh_3} + 2\mathrm{Ni(acac)_2} + \mathrm{H_2O} \rightarrow [\mathrm{Ni(acac)_2(Ph_3SnOH)}]_2 \quad (4)$$

$$2\mathrm{Ph_3SnO_2CCH_3} + 2\mathrm{Ni(acac)_2} + 2\mathrm{H_2O} \rightarrow [\mathrm{Ni(acac)_2(Ph_3SnOH)}]_2 + 2\mathrm{CH_3CO_2H} \quad (5)$$

Suitable crystals for X-ray diffraction studies of **2** were grown by slowly diffusing hexane into a THF solution of the complex. An ORTEP representation of the observed structure is shown in Figure 2. Due to the crystallographic center of symmetry, only the bond distances and angles in half of the molecule are listed in Table 2. As can be seen, the tetrametallic compound is formed by two fragments, Ni(acac)$_2$(Ph$_3$SnOH), as expected, with bridging by the oxygen atoms of the acetylacetonate. The bridging plane is oriented parallel and is coplanar with the Ni$_2$O$_2$ bridging plane. Accordingly, the complex should exhibit antiferromagnetic coupling (Ni-Ni = 3.18 Å)[20] in the same manner as the isostructural isopropanol adduct [Ni(acac)$_2$(i-C$_3$H$_7$OH)]$_2$[21] or the complex [Co(acac)$_2$(H$_2$O)]$_2$.[12] Two intramolecular hydrogen bonds (2.912 Å) in **2** exist between the hydrogen of the hydroxide of R$_3$SnOH and one oxygen atom of the nonbridging acetylacetonate ligand. The coordinated Ph$_3$SnOH in **2** has a distorted tetragonal environment with short Sn−O−bonds (1.98 Å). In contrast, uncoordinated triphenyltin hydroxide crystallizes in a polymeric chain with a five-coordinate [C$_3$O$_2$] core.[22] Thus, the Sn−O bonds in the latter compound are expanded (2.20 and 2.25 Å).

Conclusions

Novel M(acac)$_2$ adducts containing PhHgOHgPh and Ph$_3$SnOH ligands have been prepared. Compound **1** is an intermediate in the catalytic symmetrization of PhHgOH by M(acac)$_2$. PhHgOHgPh is formed in a metal(II) coordination sphere and is activated to undergo the symmetrization reaction, in which HgPh$_2$ and HgO are formed. We are continuing our studies of the utility of coordination compounds in the stabilization intermediates of organometallic reactions.

Experimental Section

Materials and Procedures. Ni(acac)$_2$, Co(acac)$_2$, and the pyridine adduct Ni(acac)$_2$(py)$_2$ were prepared as described in the literature.[23] Arylmercuric hydroxides were synthesized either from the arylmercuric halides[24] or the acetates[10] according to the literature procedures.[25] All other reagents were obtained commercially and used as supplied. All experiments were carried out under argon by standard Schlenk techniques. Solvents were purified by standard methods. IR spectra (4000−450 cm^{-1}) were recorded on a Perkin-Elmer 2000 FT-IR spectrometer in Nujol mulls between KBr disks. NMR spectra were recorded at room temperature on a Bruker AC 200F spectrometer (^{1}H, 200 MHz; ^{13}C, 50 MHz). Elemental analyses were carried out on a Carlo-Erba 1106 Elemental Analyser (Erlangen, Germany) or on a Leco CHNS-932 Elemental Analyser (Jena, Germany).

Preparation of [Ni(acac)$_2$(PhHgOHgPh)(Et$_2$O)]$_2$ (1c) from PhHgOH. PhHgOH (2.3 g, 7.8 mmol) was added to a solution of Ni(acac)$_2$ (1.0 g, 3.9 mmol) or Ni(acac)$_2$(py)$_2$ (1.6 g, 3.9 mmol) in 20 mL of THF. After an ultrasonic treatment for 30 min at room temperature, the solvent was evaporated in vacuo. The residue was extracted with 30 mL of ether, and the extract was filtered through a bed of Celite. The filtrate was concentrated to approximately 10 mL. Cooling to −20 °C afforded green crystals overnight, which were isolated by decanting and washed with several portions of cold ether. Yield: 2.7 g, 78%. Anal. Calcd for C$_{52}$H$_{68}$O$_{12}$Ni$_2$Hg$_4$: C, 34.96; H, 3.81. Found: C, 34.09; H, 3.62. IR (cm^{-1}): 3068, 3061 (ν_{CH}, Ph), 1584 ($\nu_{\mathrm{C=O}}$), 1516 ($\delta_{\mathrm{CH_3}}$, acac), 728, 699 (δ_{CH}, Ph), 670 ($\nu_{\mathrm{as},\mathrm{Hg-O-Hg}}$).

Preparation of [Ni(acac)$_2$(PhHgOHgPh)(Et$_2$O)]$_2$ (1c) from PhHgCl. To a solution of PhHgCl (1.5 g, 4.8 mmol) in 50 mL of THF was added NaOH (0.19 g, 4.8 mmol) and 5 mL of water. The resulting mixture was heated at reflux for 1 h. After filtration through a bed of Celite, Ni(acac)$_2$ (0.62 g, 2.4 mmol) was added and the solution was treated by ultrasound for 30 min. Workup identical with that above gave **1c** as green crystals. Yield: 1.45 g, 67%. Anal. Found: C, 34.48; H, 3.70.

Preparation of [Ni(acac)$_2$(PhHgOHgPh)]$_2$ (1b). Heating compound **1c** in vacuo at 50 °C resulted in loss of Et$_2$O

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and gave a green, microcrystalline product: Anal. Calcd for $C_{44}H_{48}O_{10}Ni_2Hg_4$: C, 31.90; H, 2.92. Found: C, 31.76; H, 2.82.

Preparation of [Co(acac)$_2$(PhHgOHgPh)]$_2$ (1a). With 2.3 g of PhHgOH and 1.0 g of Co(acac)$_2$ as starting materials, the same procedure provided 2.0 g (63% yield) of pink microcrystals. Anal. Calcd for $C_{44}H_{48}O_{10}Co_2Hg_4$: C, 31.90; H, 2.92. Found: C, 31.83; H, 2.83.

Synthesis of HgPh$_2$ via 1c. Compound **1c**, 0.5 g (0.28 mmol), was sublimed at 200 °C and atmospheric pressure to yield 0.17 g (85%) of HgPh$_2$. Mp: 121 °C (lit.[26] mp 121−122 °C). Anal. Calcd for $C_{12}H_{10}Hg$: C, 40.61; H, 2.82. Found: C, 40.58; H, 2.79. ^{13}C NMR ($CDCl_3$, 25 °C): δ 170.44 (C−Hg), 137.55, 128.63, 128.27 (aryl).[27] IR (cm^{-1}): 1574 ($\nu_{C=C}$), 736, 732, 696 (δ_{CH}, Ph).

Catalytic Symmetrization of HgPh$_2$. Procedure A. A mixture of PhHgCl (6.3 g, 20 mmol) in toluene (50 mL) and NaOH (0.8 g, 20 mmol) in water (20 mL) was heated at reflux for 30 min. After separation of the aqueous phase, Ni(acac)$_2$ (0.1 g, 0.4 mmol) was added and the mixture was again heated in refluxing toluene. After 3 h, a yellow solution was obtained. Flash chromatography (silica, 2:1 toluene/acetone) provided 2.4 g (66%) of HgPh$_2$. Anal. Found: C, 40.57; H, 2.81.

Procedure B. A mixture of $PhHgO_2CCH_3$ (3.0 g, 9.0 mmol) in toluene (40 mL) and NaOH (0.36 g, 9.0 mmol) in water (10 mL) was heated at reflux for 1 h. The preceding reaction and workup identical with that as described in procedure A gave 1.1 g (70%) of HgPh$_2$. Anal. Found: C, 40.55; H, 2.78.

Procedure C. A solution of PhHgSH[24] (1.8 g, 5.8 mmol) and 0.05 g of Ni(acac) was stirred in 30 mL of toluene at ambient temperature. After 2 days HgS had precipitated quantitatively. The mixture was filtered, and the filtrate was concentrated in vacuo to provide 0.8 g (83%) of HgPh$_2$. Anal. Found: C, 40.60; H, 2.82.

(p-CH$_3$O-C$_6$H$_4$)$_2$Hg. Following the procedure A described above for HgPh$_2$ with p-CH_3O-C_6H_4HgCl (2.0 g, 5.8 mmol), NaOH (0.23 g, 5.8 mmol), and 0.05 g of Ni(acac)$_2$ gave (p-CH_3O-C_6H_4)$_2$Hg (0.95 g, 79%). Mp: 204 °C (lit.[28] mp 202 °C). Anal. Calcd for $C_{14}H_{14}O_2Hg$: C, 40.53; H, 3.40. Found: C, 40.43; H, 3.46. ^1H NMR ($CDCl_3$): δ 7.36 (d, 2H, J = 8.4 Hz, m-CH),7.01 (d, 2H, J = 8.4 Hz, o-CH), 3.81 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$, 25 °C): δ 162.34 (C−Hg), 159.55 (C−OCH_3), 138.28, 114.31 (aryl), 55.05 (OCH_3). IR (cm^{-1}): 1586, 1564 ($\nu_{C=C}$), 817, 808, 789 (δ_{CH}, aryl).

(p-CH$_3$-C$_6$H$_4$)$_2$Hg. Following the procedure A with p-CH_3-C_6H_4HgCl (1.9 g, 5.7 mmol), NaOH (0.23 g, 5.7 mmol), and Ni(acac)$_2$ (0.05 g) gave (p-CH_3-C_6H_4)$_2$Hg (0.92 g, 83%). Mp: 246 °C (lit.[29] Mp 244 °C). Anal. Calcd for $C_{14}H_{14}Hg$: C, 43.92; H, 3.69. Found: C, 43.72; H, 3.76. ^1H NMR ($CDCl_3$): δ 7.44 (d, 2H, J = 7.4 Hz, m-CH), 7.17 (d, 2H, J = 7.4 Hz, o-CH), 2.30 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 25 °C): δ 167.20 (C−Hg), 138.18, 136.94, 129.54 (aryl), 20.98 (CH_3). IR (cm^{-1}): 1592, 1493 ($\nu_{C=C}$), 792 (δ_{CH}, aryl).

Hg(p-C$_6$H$_4$N═CHPh)$_2$. Following the procedure B with p-PhHC═N-$C_6H_4HgO_2CCH_3$ (2.5 g, 5.7 mmol), synthesized by heating of 2.0 g (5.7 mmol) of p-H_2N-$C_6H_4HgO_2CCH_3$ and 0.58 mL (5.7 mmol) of benzaldehyde in refluxing methanol in quantitative yield, 0.23 g (5.7 mmol) of NaOH, and Ni(acac)$_2$ (0.05 g) gave 0.45 g (28%) of Hg(p-C_6H_4N═CHPh)$_2$. Mp: 181 °C (lit.[30] Mp 180 °C). Anal. Calcd for $C_{26}H_{20}N_2Hg$: C, 55.66; H, 3.59; N, 4.99. Found: C, 55.61; H, 3.56; N, 4.95. ^1H NMR ($CDCl_3$): δ 8.46 (s, 1H, CH), 7.24−7.93 (m, 9H, aryl). ^{13}C NMR ($CDCl_3$): δ 168.22 (C−Hg), 160.34 (CH═N), 151.95 (C−N), 138.07, 136.34, 131.35, 128.85, 128.76, 121.01 (aryl). IR (cm^{-1}): 1621 ($\nu_{C=N}$), 1570, 1447 ($\nu_{C=C}$), 819, 755, 717, 692 (δ_{CH}, aryl).

[Ni(acac)$_2$(Ph$_3$SnOH)]$_2$ (2). To a solution of Ni(acac)$_2$ (1.0 g, 3.9 mmol) in 50 mL of THF was added 3.9 mmol of the appropriate organotin compound Ph_3SnOR' (a, R′ = H; b, R′ = CH_3CO, c, R′ = $SnPh_3$). In addition, using b or c 3.9 mmol of water was added. After an ultrasonic treatment for 30 min at room temperature the reaction mixture was filtered through Celite. The filtrate was concentrated to approximately 20 mL, and 10 mL of n-hexane was added. Cooling to −20 °C overnight afforded green crystals. Yield: 1.7 g, 70%. Anal. Calcd for $C_{56}H_{60}O_{10}Ni_2Sn_2$: C, 53.90; H, 4.85. Found: C, 53.85; H, 4.89. IR (cm^{-1}): 3339 (ν_{OH}), 3065, 3048 (ν_{CH}, Ph), 1595 ($\nu_{C=O}$), 1518 (δ_{CH_3}, acac), 731, 698 (δ_{CH}, Ph).

X-Ray Structure Determinations. X-ray diffraction data were collected on a Phillips PW1100 four-cycle automatic diffractometer with graphite-monochromated Ag Kα radiation (λ = 0.560 142 Å). The crystals were embedded in a drop of fast-hardening adhesive (**1c**) or sealed inside a glass capillary (**2**). The structures were solved by direct methods (SHELXS-86)[31] and refined by full-matrix least-squares techniques against F^2 (SHELXL-93).[32] An absorption correction for compound **1c** was based on ψ-scan solution. Hydrogen atom contributions were calculated but not refined. In the final cycles all non-hydrogen atoms, except the solvent in **1c**, were refined anisotropically. The carbon atom positions of the third phenyl group in compound **2** had to be split because of disorder. The program XP (Siemens Analytical X-ray Instruments, Inc.) was used for structure representation.

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Supporting Information Available: Details of the structure determinations, including tables of atomic coordinates, bond distances and angles, and thermal parameters for **1c** and **2**, and characterization data for arylmeruric hydroxides (17 pages). Ordering information is given on any current masthead page.

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