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New Chiral Palladacycles from an Unprecedented Cyclopalladation of Cyclobutadiene-Bound Phenyl Groups of Cobalt Sandwich Compounds

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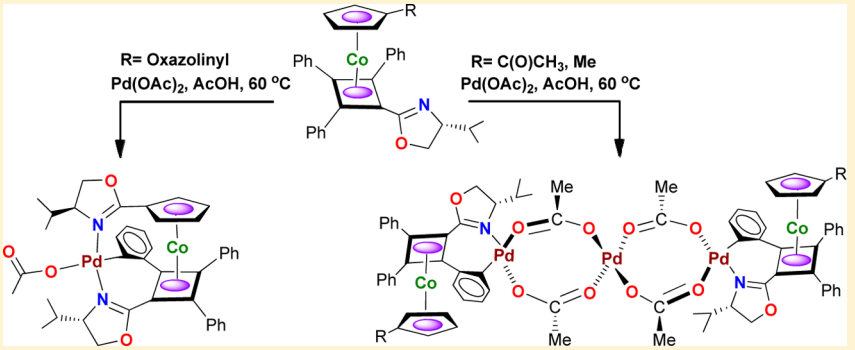
Supporting Information



ABSTRACT: Reaction of in situ generated $\{\eta^5$-[MeOC(O)]$C_5H_4\}$Co$(PPh_3)_2$ with methyl 3-phenyl-2-propynoate followed by diphenylacetylene in refluxing toluene resulted in the formation of the cobalt sandwich compound $\{\eta^5$-[MeOC(O)]$C_5H_4\}$Co$\{\eta^4$-C_4Ph_3[C(O)OMe]} (**1**), having methyl ester units on both the cyclopentadienyl (Cp) and cyclobutadiene (Cb) rings. Hydrolysis of the ester groups using aqueous KOH resulted in the dicarboxylic acid $\{\eta^5$-C_5H_4[C(O)OH]}Co$\{\eta^4$-C_4Ph_3[C(O)OH]} (**2**). The dicarboxylic acid **2** was converted to the novel bis(oxazolinyl) derivative [η^5-(4-*i*Pr-2-Ox)C_5H_4]Co[η^4-C_4Ph_3(4-*i*Pr-2-Ox)] (**3**; Ox = oxazolinyl) by its reaction with oxalyl chloride, (*S*)-2-amino-3-methyl-1-butanol, triethylamine, and mesyl chloride. Reaction of the chiral bis(oxazoline) ligand **3** with $Pd(OAc)_2$ in acetic acid at 60 °C resulted in the formation of the novel chiral palladacycle **4**, resulting from an unprecedented cyclopalladation involving one of the cyclobutadiene-bound phenyl groups. Palladacycle **4** has two *trans*-oriented oxazolinyl units and one of the phenyl groups of the cyclobutadiene ring bound to the palladium center along with an acetyl group. The reaction of KX (X = Br, I) with **4** in acetone−water medium yielded the bromo- and iodo-derived chiral palladacycles **5a,b**. Compounds analogous to **3** having a chiral oxazolinyl unit on the Cb ring and a methyl or acetyl unit on the Cp ring, (η^5-RC_5H_4)Co(η^4-C_4Ph_3R') (R′ = oxazolinyl; R = acetyl (**8a**), methyl (**8b**)) were also prepared and characterized. Analogous reactions of **8a,b** with 1.5 equiv of $Pd(OAc)_2$ in acetic acid at 60 °C gave the chiral palladacycles **9a,b.** Analysis of these compounds indicated that, in contrast to the monomeric chiral palladacycle obtained from the reaction of **3**, compounds **9a,b** are molecules with a unique linear tetraacetate-bridged tripalladium core having the two cyclopalladated cobalt sandwich units at the periphery. Structural analysis of **9a** indicated that the molecule possesses the same type of seven-membered palladacycle observed in the cases of **4** and **5a,b**.

INTRODUCTION

Among metal sandwich compounds, one of the best competitors for ferrocene with regard to stability, ease of synthesis, and reaction chemistry is the 18-electron cobalt sandwich compound [(η^5-Cp)Co(η^4-C_4Ph_4)].[1] While the molecule as such is much less reactive than ferrocene, its cyclopentadienyl derivatives, especially the carboxylate ester, have shown excellent potential for developing novel chiral organometallic compounds for asymmetric catalysis ably assisted by the bulky tetraphenylcyclobutadiene moiety.[2] The electron donor capability of this sandwich compound has also been utilized for realizing new luminescent materials and photovoltaic devices.[3] To date, the chemistry centered on this molecule has been mostly focused on derivatizing the cyclopentadienyl group with one or more functional substituents.[1a,2a,4] The phenyl groups on the cyclobutadiene ring have remained passive to all such reactions carried out on the cyclopentadienyl ring, except for an acylation performed on $\{\eta^5$-[MeOC(O)]$C_5H_4\}$Co(η^4-C_4Ph_4) by Richards and coworkers.[5] The steric bulkiness of these cyclobutadiene-bound phenyl groups has also been extended by Gandon and coworkers: however, starting with a tetrakis(4-bromophenyl) derivative of (η^5-Cp)Co(η^4-C_4Ph_4).[6]

Monomeric and dimeric palladacycles based on (η^5-Cp)Co(η^4-C_4Ph_4) and [(η^5-Cp)Co(η^4-C_4Ph_3)]$_2$ are well documented,

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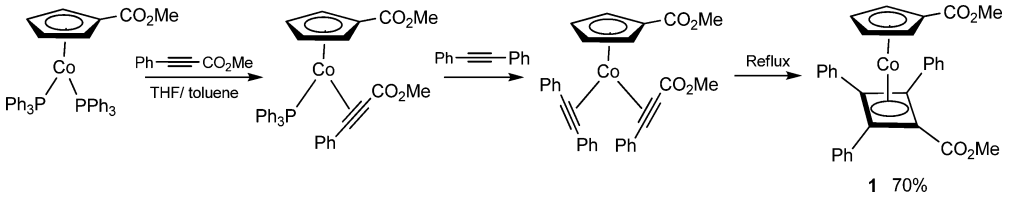
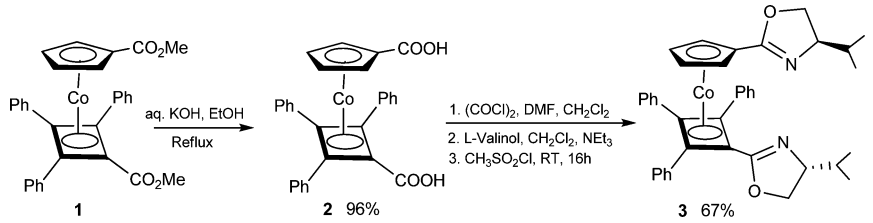
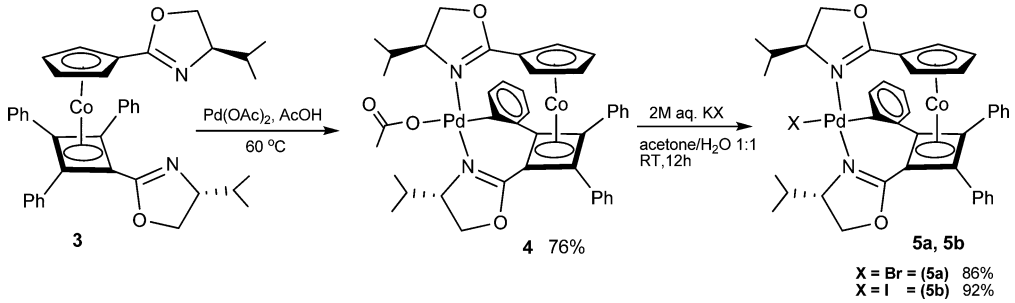
Scheme 1. Synthesis of the Diester Derivative 1 of the Cobalt Sandwich Compound



Scheme 2. Synthesis of Dicarboxylic Acid 2 and the Bis(oxazoline)-Derived Cobalt Sandwich Compound 3



Scheme 3. Synthesis of the Chiral Bis(oxazolinyl) Palladacycles 4 and 5a,b



with established utility in homogeneous asymmetric catalysis.[7,8] However, all of these cobalt sandwich based palladacycles had the chiral binding moiety positioned on the cyclopentadienyl ring and the palladacycles were formed from a C−H activation followed by cyclopalladation of cyclopentadienyl-bound protons. We introduce herein a new type of $[(\eta^5\text{-RCp})\text{Co}(\eta^4\text{-}C_4Ph_3R')]$ type bis(oxazoline) compound having chiral oxazolinyl units on both the cyclobutadiene and cyclopentadienyl rings of the cobalt sandwich compound. We report the formation of a palladacycle resulting from the cyclopalladation of one of the cyclobutadiene-bound phenyl groups of the cobalt sandwich compound. This kind of ortho palladation, involving cyclobutadiene-bound phenyl groups, is unprecedented in the chemistry of CpCoCb (Cb = cyclobutadiene) type sandwich compounds.[9] We also report the synthesis of mono(oxazoline)-derived CpCoCb type compounds having the chiral oxazoline unit bound only to the cyclobutadiene ring and show their differences in palladacycle formation in comparison to the bis(oxazoline)-derived sandwich compounds, resulting in unique linear tripalladium complexes bridged by acetate groups and flanked by the palladacycles at the periphery.

RESULTS AND DISCUSSION

$\{\eta^5\text{-}[\text{MeOC(O)}]C_5H_4\}\text{Co}\{\eta^4\text{-}C_4Ph_3[\text{C(O)OMe}]\}$ (**1**), the diester derivative of the cobalt sandwich compound, was prepared by the stepwise addition of methyl 3-phenyl-2-propynoate and diphenylacetylene to in situ prepared $\{\eta^5\text{-}[\text{MeOC(O)}]C_5H_4\}\text{Co}(PPh_3)_2$ (Scheme 1). Compound **1** was hydrolyzed to its dicarboxylic acid **2** by refluxing with aqueous KOH in ethanol. The dicarboxylic acid, by its reaction with oxalyl chloride followed by (*S*)-2-amino-3-methyl-1-butanol, triethylamine, and mesyl chloride, was converted to $[\eta^5\text{-}(4\text{-}i\text{Pr-}2\text{-Ox})C_5H_4]\text{Co}[\eta^4\text{-}C_4Ph_3(4\text{-}i\text{Pr-}2\text{-Ox})]$ (**3**; Ox = oxazolinyl) (Scheme 2). Reaction of the bis(oxazoline) complex **3** with palladium acetate in acetic acid at 60 °C resulted in the novel palladacycle **4**, where one of the phenyl groups bound to the cyclobutadiene ring was found to get ortho-palladated, forming a novel seven-membered palladacycle (Scheme 3).

The identity of the palladacycle **4** was conclusively proved by single-crystal X-ray diffraction analysis (Figure 2) and NMR spectral analysis. ^{1}H and ^{13}C NMR analysis of **4** in the crude and in the crystalline form also revealed that **4** is a single compound. Palladacycle **4** was found to be optically active with a specific rotation, $[\alpha]_D^{35} = +160°$. The acetate group of the palladacycle **4** was replaced by bromo and iodo groups by reacting with KBr and KI in acetone−water medium to give chiral palladacycles **5a** ($[\alpha]_D^{35} = +175°$) and **5b** ($[\alpha]_D^{35} = +197°$) (Scheme 3). The palladacycles **4** and **5a,b** were found to be soluble in solvents such as chloroform, dichloromethane, ethyl acetate, and tetrahydrofuran and were also found to be highly stable to air and moisture.

Since both the cyclopentadienyl- and cyclobutadiene-bound oxazolinyl groups along with a terminal acetate ligand were involved in the palladacycle formation of **4**, we were keen to see if an analogous aryl C−H activation and subsequent cyclopalladation of the phenyl group could be brought about in the absence of the Cp-bound oxazolinyl group. A cyclopentadienyl-unsubstituted analogue of **3** was prepared. However, its reaction with $Pd(OAc)_2$ resulted in a yellow solid which was highly insoluble in common organic solvents. With a view to increase solubility, we prepared the chiral oxazolines **8a,b**,

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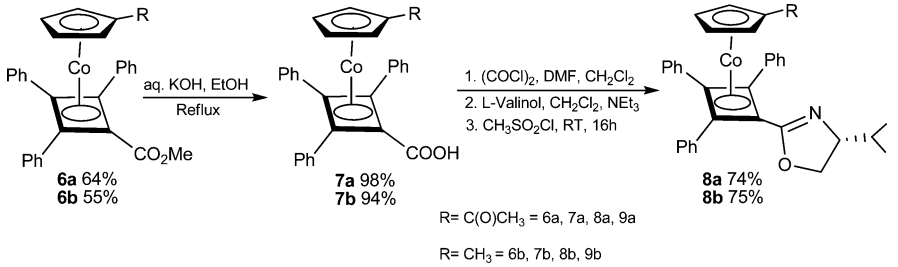
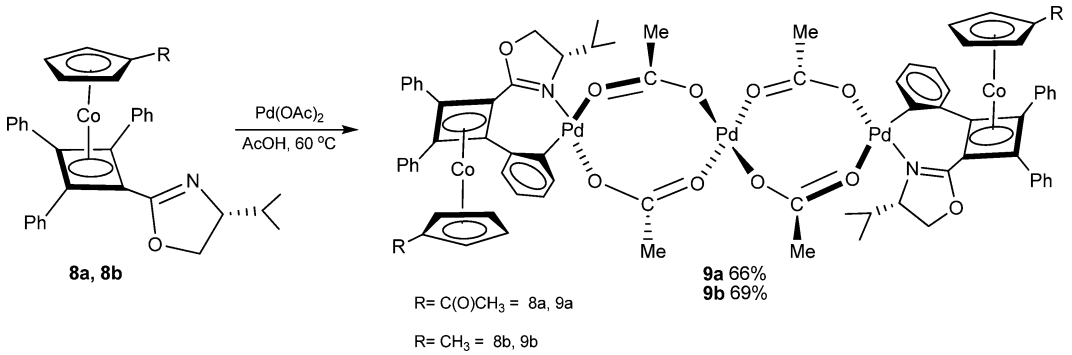
Scheme 4. Synthesis of Mono(oxazoline) Derivatives 8a,b Having the Chiral Oxazoline Unit Bound Only to the Cyclobutadiene Ring



Scheme 5. Synthesis of Tetraacetate-Bridged Tripalladium Complexes 9a,b Having the Cyclopalladated Cobalt Sandwich Units at the Periphery



having acetyl and methyl groups bound to the Cp ring, respectively (Scheme 4).

In total contrast to the reaction of **3**, reaction of **6a** with palladium acetate in acetic acid resulted in complex **9a**, having an unusual linear tetraacetate-bridged tripalladium core with two cyclopalladated cobalt sandwich units flanking both ends (Scheme 5). Irrespective of the stoichiometry of compound **8a** and palladium acetate used in the reaction, the same compound was found to form, but the best yield (66%) resulted from a 2:3 molar ratio reaction. Due to the poor quality of the crystals, the structure of **9a** could not be solved. However, an exactly identical reaction was shown by **8b**, having a methyl-substituted Cp ring, resulting in the tripalladium complex **9b** in 69% yield, whose crystal structure was determined (Figure 5). Interestingly, similar to compound **4**, the seven-membered palladacycle formation resulting from phenyl cyclopalladation was found to happen on both the cobalt sandwich units of this compound as well. The tripalladium complexes **9a,b** were both found to be optically active with specific rotations: $[\alpha]_D^{35}$ = −30.6 and −26.5°, respectively. The structure of **9b** shows similarity to a tripalladium complex reported by Moyano and co-workers from a reaction of oxazolinyl ferrocene and palladium acetate carried out in benzene medium.[10] In contrast to the seven-membered palladacycle observed in this study, their tripalladium complex showed a six-membered palladacycle having both palladium and iron as part of the ring.

Recent reports from our group on the palladium complex of 1,3-cyclopentadienyl bis(oxazoline)-derived [(η^5-C_p)Co(η^4-C_4Ph_4)] and chiral palladacycles derived from cyclobutadiene-bridged dimeric cobalt sandwich compounds have shown excellent enantioselectivity for the Overman−Claisen rearrangement of trichloroacetimidates.[7b,8] However, analogous catalysis attempted with the chiral palladacycles **4** and **5a,b** did not show any enantioselectivity, This observation supports the theoretical and kinetic studies carried out by Overman and co-workers on the importance of basal bulkiness of the sandwich compounds for realizing enantioselectivity in catalysis involving cobalt oxazolinyl palladacycles.[11]

NMR Spectral Studies. Quite interestingly, both the monomeric bis(oxazoline)-derived palladacycles (**4** and **5a,b**) and the mono(oxazoline)-based palladacycles having a tripalladium core (**9a,b**) showed very similar ^{1}H NMR peak splitting patterns for the aryl protons (see the Supporting Information), confirming the similarity of the palladacycle ring formation. In addition, a decrease of one unit was observed in the integration of the phenyl groups of these palladacycles in comparison to their parent oxazoline-derived sandwich compounds. While all the phenyl protons of the bis(oxazoline) **3** appear in the range 7.05−7.71 ppm, spectra of the palladacycles derived from **3** showed further splitting and a noticeable upfield shift to 6.65−6.98 ppm for three of the aryl protons. Quite similar splitting of the phenyl protons was observed in the ^{1}H NMR spectra of compounds **9a,b**, which indicated that the same cyclopalladation has happened in these compounds as well. The palladium-bound carbon atoms in the ^{13}C NMR spectra of **4**, **5a,b**, and **9a,b** showed a downfield shift to 138.20−147.03 ppm, in comparison to other phenyl carbon atoms, which appeared in the range 122.97−130.06 ppm. Such downfield shifts of palladium-bound carbon atoms of phenyl groups have been reported for five-membered phenyl-bound palladacycles.[12] The ^{13}C NMR for the carbonyl carbon of the terminal acetate group bound to the palladium of palladacycle **4** appeared at 177.25 ppm, similar to the case for {[η^5-(4-*i*Pr-2-Ox)Cp]Co(η^4-C_4Ph_3)}$_2$PdOAc, where it was observed at 176.62 ppm.[8a] The two carbonyl carbon peaks of the four bridging acetate units were observed at 182.54−184.13 ppm in compounds **9a,b**. These values for bridging acetate groups are akin to those reported for the ferrocene-derived tripalladium complexes, where they were observed at 181.70−184.40 ppm.[10]

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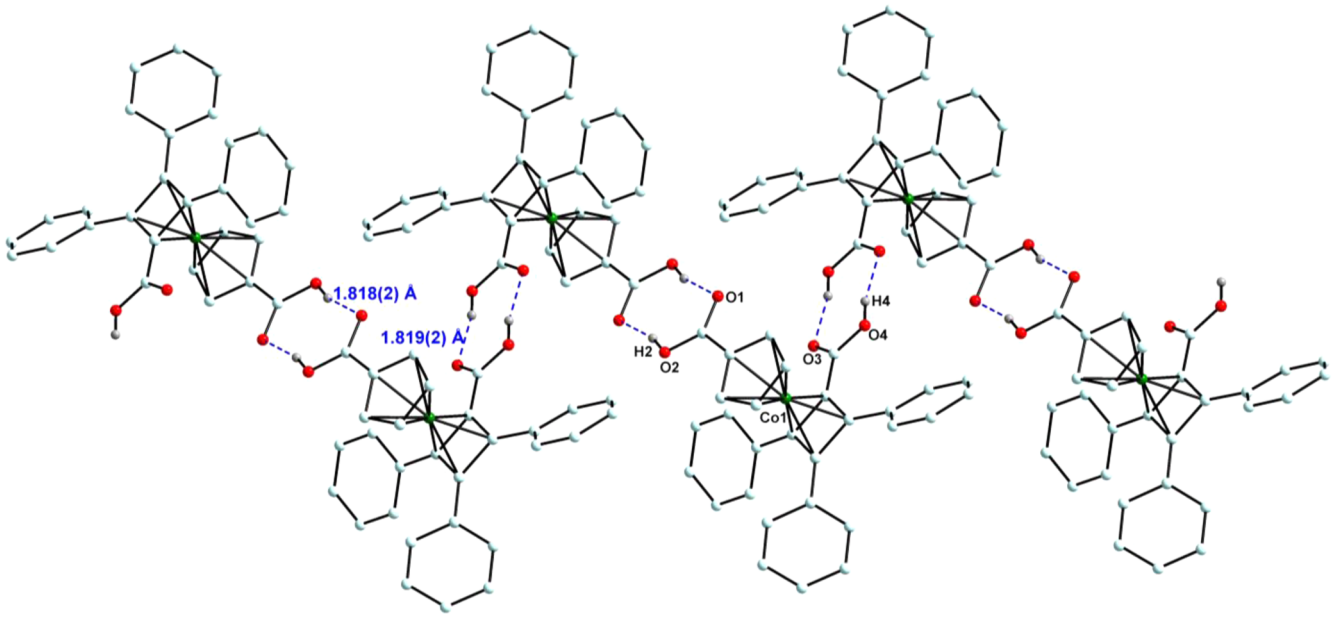

Figure 1. Molecular structure of the compound **2** showing the intermolecular hydrogen bonding.

X-ray Crystal Structures of Compounds 2, 4, 5b, 7a, and 9b. Molecular structures of the compounds **4**, **5b**, and **9b** and crystal-packing diagrams of the compounds **2** and **7a** are given in Figures 1−5 (molecular structures of compounds **2** and **7a** are given in the Supporting Information). Structural analysis of the dicarboxylic acid **2** shows an interesting selectivity in the intermolecular hydrogen bonding shown by the two carboxylic acid groups. The carboxylic acid group of the Cp ring is connected specifically to the carboxylic acid group of the Cp ring belonging to another molecule. A similar selectivity in binding is observed for the carboxylic acid group bound to the Cb rings, resulting in a zigzag-chain-like arrangement of the molecules with the tetraphenylcyclobutadiene units placed at the periphery of this chain (Figure 1). Unlike the hydrogen bonding observed in **2** which resulted in this polymeric assembly, the hydrogen bonding observed in the reported crystal structures of both ferrocene-1,1′-dicarboxylic acid and ruthenocene-1,1′-dicarboxylic acid resulted only in dimeric units.[13] The crystal structure of the palladacycle **4** (Figure 2) shows a square-planar palladium center to which the two isopropyl-substituted *trans*-oriented oxazolinyl units are attached at an angle of 162.9(2)°. The acetate group is found to be located anti (177.6(2)°) to the cyclopalladated carbon of the phenyl ring. In contrast, the reported crystal structure of a very similar 1,1′-bis(oxazolinyl)ferrocene-based palladium dichloride complex shows a *cis* orientation of the two oxazolinyl groups.[14] More interestingly, no C−H activation and palladacycle formation was observed for this ferrocene-derived complex. A comparison of the crystal structures of the two bis(oxazoline) palladacycles **4** and **5b** (Figure 3) showed some minor variations. The angle formed by the cyclopalladated carbon with palladium and acetate (C(22)−Pd(1)−O(3)) was found to be more linear (177.6(2)°) in comparison to the corresponding angle (C(25)−Pd(1)−I(1)) of the iodo complex (169.8(8)°).

The hydrogen bonding observed in the case of **7a** (Figure 4) interestingly shows dimer formation, but instead of two carboxylic acid groups forming a hydrogen bond, which is the normal feature of carboxylic acid hydrogen bonds, the acid

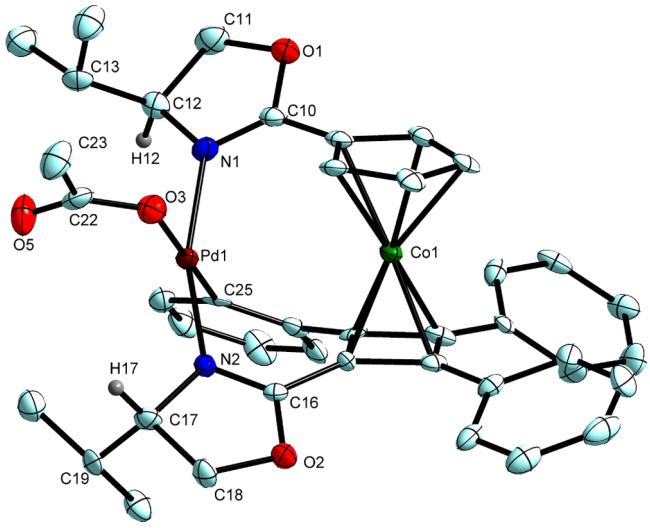

Figure 2. Molecular structure of chiral palladacycle **4.** Thermal ellipsoids are drawn at the 30% probability level. Some hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−C(25), 1.987(5); Pd(1)−N(1), 2.043(5); Pd(1)−N(2), 2.030(5); Pd(1)−O(3), 2.138(4); C(25)−Pd(1)−N(2), 92.1(2); C(25)−Pd(1)−N(1), 85.5(2); N(2)−Pd(1)−N(1), 162.9(2); C(25)−Pd(1)−O(3), 177.6(2); N(2)−Pd(1)−O(3), 90.1(2); N(1)−Pd(1)−O(3), 92.7(2).

group of the cyclobutadiene ring is involved in hydrogen bonding with the acetyl group of the cyclopentadiene ring and vice versa. The crystal structure of the palladacycle **9b** (Figure 5) shows a tripalladium core bridged by four acetate groups having the phenyl cyclopalladated cobalt sandwich units at the periphery. There are interesting structural features of the tripalladium compound **9b** that are noticeable. The three palladium atoms show an almost linear arrangement with a departure from linearity of 9.1°. The departure from linearity observed in the only other reported example of a tetraacetate-bridged tripalladium complex is 1.1°, which is a ferrocene-based complex.[10] The Pd−Pd bond distance of 2.980(1) Å observed

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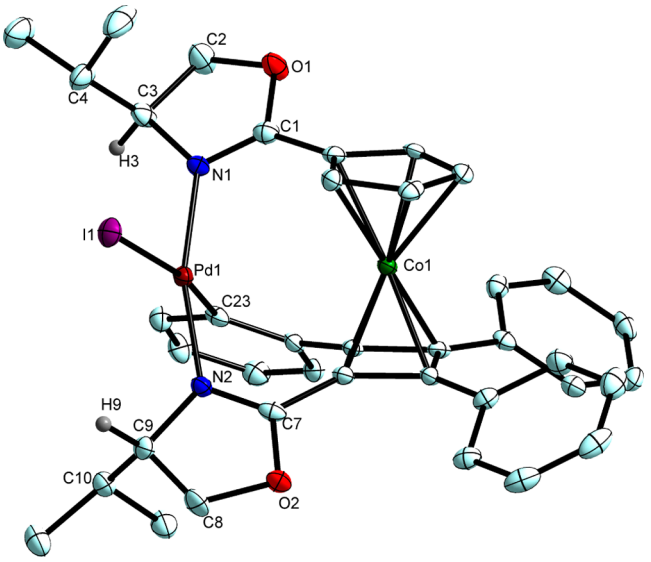

Figure 3. Molecular structure of chiral palladacycle **5b.** Thermal ellipsoids are drawn at the 30% probability level. Some hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−C(23), 2.003(3); Pd(1)−N(2), 2.016(2); Pd(1)−N(1), 2.034(2); Pd(1)−I(1), 2.769(4); C(23)−Pd(1)−N(2), 88.7(1); C(23)−Pd(1)−N(1), 85.7(1); N(2)−Pd(1)−N(1), 164.0(9); C(23)−Pd(1)−I(1), 169.8(8); N(2)−Pd(1)−I(1), 90.1(7); N(1)−Pd−I(1), 98.1(7).

in **9b** is appreciably shorter than that observed in the reported ferrocene-based tripalladium complex (3.046(5) Å). The two sandwich units in **9b** are not *trans* to each other, as the angle between Cp rings of the two sandwich units is 67.3(4)°.

CONCLUSIONS

In conclusion, we report the first synthesis of cobalt sandwich compounds of the type (η^5-RCp)Co(η^4-C_4Ph_3R') having chiral oxazolinyl groups on the cyclobutadiene ring alone as well on both the cyclopentadienyl and cyclobutadiene rings. Reaction of the bis(oxazoline)-derived sandwich compound with Pd(OAc)$_2$ led to the formation of the novel monomeric chiral palladacycle **4**, resulting from an unprecedented cyclopalladation of one of the phenyl groups bound to the cyclobutadiene ring. In contrast, the reaction between the mono(oxazoline) derivative of the cobalt sandwich compounds **8a**,**b** with Pd(OAc)$_2$ led to linear tetraacetate-bridged tripalladium compounds with cyclopalladated cobalt sandwich units at the periphery. Formation of palladacycles **4**, **5a**,**b**, and **9a**,**b** indicate the first observation of C−H activation followed by ortho palladation involving phenyl groups bound to the cyclobutadiene ring of CpCoCb type cobalt sandwich compounds. To the best of our knowledge, compounds **4** and **5** are also the first examples of transition-metal complexes based on the η^5-CpCo(η^4-C_4R_4) scaffold where functional groups present on both the Cp and Cb rings of the sandwich compound are involved in coordination as a chelating bidentate ligand, thus opening up a new class of cobalt sandwich based bidentate ligands similar to 1,1′-bis(oxazolinyl)ferrocene and dppf.

EXPERIMENTAL SECTION

General Methods. All manipulations of the complexes were carried out using standard Schlenk techniques under a nitrogen atmosphere. All solvents were freshly distilled and used. The sodium salt of carbomethoxycyclopentadiene[15] and tris(triphenylphosphine) cobalt chloride[16] were prepared according to literature procedures. Dimethyl carbonate, triphenylphosphine (Spectrochem), L-valinol, mesyl chloride, and methyl phenylpropiolate (Alfa Aesar) were used as received.

Instrumentation. ^{1}H and ^{13}C{^{1}H} spectra were recorded on a Bruker Spectrospin DPX-300 NMR spectrometer at 300 and 75.47 MHz, respectively. IR spectra in the range 4000−250 cm^{-1} were recorded on a Nicolet Protége 460 FT-IR spectrometer as KBr pellets. Elemental analyses were carried out on a Carlo Erba CHNSO 1108 elemental analyzer. Mass spectra were recorded on a Bruker Micro-TOF QII quadrupole time-of-flight (Q-TOF) mass spectrometer. Optical rotations of the chiral compounds were measured on an Autopol V (Rudolph Research, Flanders, NJ) instrument. All of the rotations were measured at 589 nm (sodium "D" line) using dichloromethane as solvent, and readings were cross-checked by taking measurements at two different concentrations.

X-ray Crystallography. Suitable crystals of compounds **2**, **4**, **5b**, **7a**, and **9b** were obtained by slow evaporation of their saturated solutions in ethyl acetate/hexane, dichloromethane/hexane, and toluene/hexane mixtures. Single-crystal diffraction studies were carried out on a Bruker SMART APEX CCD diffractometer with a Mo Kα (λ = 0.71073 Å) sealed tube. All crystal structures were solved by direct methods. The program SAINT (version 6.22) was used for integration of the intensity of reflections and scaling. The program SADABS was used for absorption correction. The crystal structures were solved and refined using the SHELXTL (version 6.12) package.[17] All hydrogen

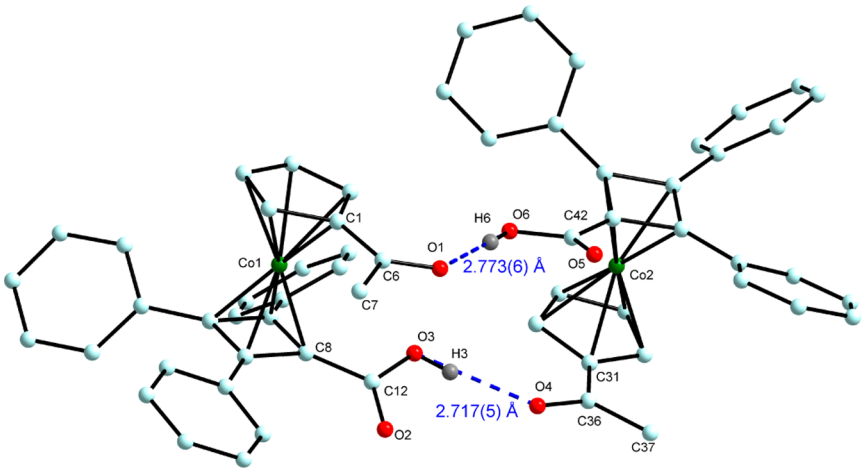

Figure 4. Molecular structure of compound **7a**, showing the intermolecular hydrogen bonding.

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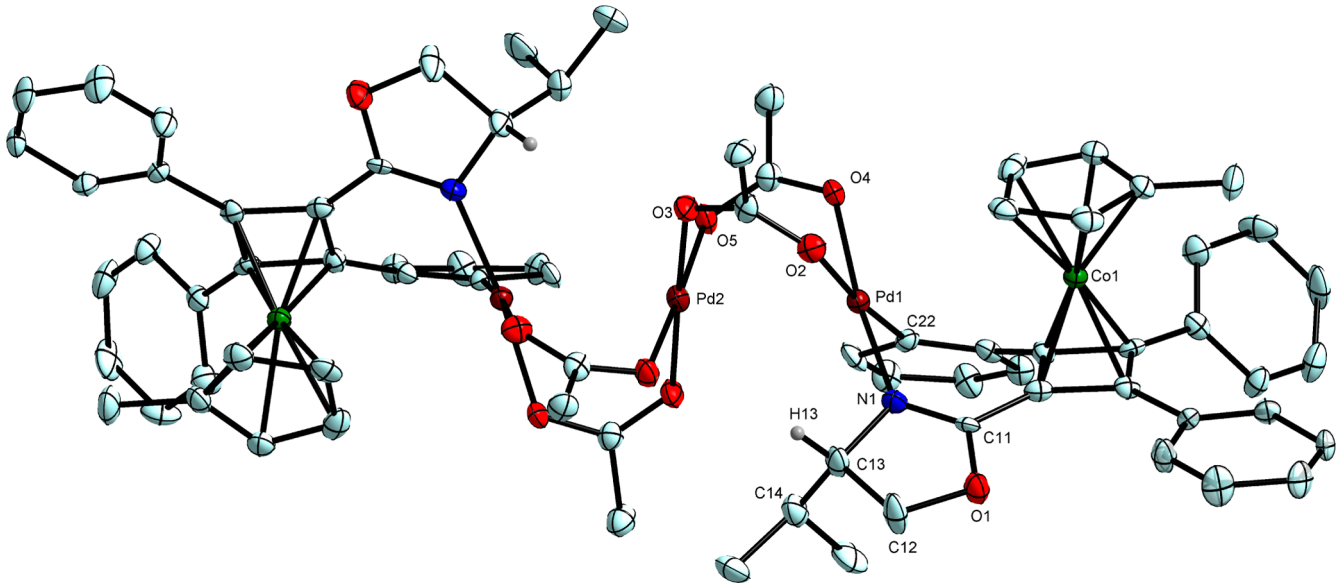

Figure 5. Molecular structure of **9b** with thermal ellipsoids at the 30% probability level. Some hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−C(22), 1.967(1); Pd(1)−N(1), 2.012(8); Pd(1)−O(2), 2.179(8); Pd(1)−O(4), 2.054(8); Pd(1)−Pd(2), 2.980(1); Pd(1)−Pd(2)−Pd(1), 170.9(6); C(22)−Pd(1)−N(1), 91.7(4); C(22)−Pd(1)−O(4), 87.6(4); N(1)−Pd(1)−O(4), 173.2(3); C(22)−Pd(1)−O(2), 175.0(4); N(1)−Pd(1)−O(2), 91.1(3); O(4)−Pd(1)−O(2), 89.2(3); C(22)−Pd(1)−Pd(2), 111.4(3).

Table 1. X-ray Crystal Structure Parameters of Compounds 2, 4, 5b, 7a, and 9b

param	2	4	5b	7a	9b
formula	$C_{29}H_{21}CoO_4$	$C_{42}H_{43}Cl_2CoN_2O_2Pd$	$C_{46}H_{46}CoIN_2O_2Pd$	$C_{30}H_{23}CoO_3$	$C_{76}H_{74}Co_2N_2O_{10}Pd_3$
mol wt	492.39	876.01	951.08	490.41	1612.43
cryst syst	triclinic	monoclinic	orthorhombic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2_1$	$P2_12_12_1$	$P2_1/n$	$P2_12_12$
a (Å)	9.802(2)	9.729(2)	13.194(2)	8.033(2)	15.803(4)
b (Å)	10.506(2)	14.665(3)	13.586(2)	29.032(8)	28.301(7)
c (Å)	12.417(2)	13.281(2)	12.268(3)	21.731(6)	9.025(2)
α (deg)	81.318(3)	90	90	90	90
β (deg)	68.052(2)	102.566(3)	90	92.532(6)	90
γ (deg)	78.993(3)	90	90	90	90
V (Å^3)	1159.9(3)	1849.5(6)	3991.5(8)	5063(2)	4036.4(2)
Z	2	2	4	8	2
T/K	298(2)	150(2)	150(2)	298(2)	150(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
ρ_{calcd} (g/cm^3)	1.410	1.573	1.583	1.287	1.327
μ (mm^{-1})	0.774	1.125	1.680	0.706	1.109
goodness of fit	1.075	1.025	1.051	1.026	1.115
θ range (deg)	1.77−25.00	1.57−24.99	1.76−25.00	1.17−25.0	1.44−25.00
total no. of rflns	6119	17826	38299	48571	38964
no. of unique rflns	4059	6500	7031	8927	7117
no. of obsd data ($I > \sigma(I)$)	3753	5814	6911	5673	5789
R_{int}	0.0272	0.0610	0.0312	0.1139	0.1042
R1, wR2 ($I > 2\sigma(I)$)[a]	0.0375, 0.1112	0.0465, 0.0977	0.0201, 0.0483	0.0682, 0.1549	0.0659, 0.1936
R1, wR2 (all data)[a]	0.0399, 0.1132	0.0535, 0.1004	0.0207, 0.0486	0.1145, 0.1712	0.0804, 0.2021
Flack param		0.00(2)	0.01(1)		0.04(5)

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \sum(|F_o|^2 - |F_c|^2)^2]\}^{1/2}$.

atoms were included in idealized positions, and a riding model was used. Non-hydrogen atoms were refined with anisotropic displacement parameters. Table 1 gives the data collection and structure solution parameters for compounds **2**, **4**, **5b**, **7a**, and **9b**. The highly distorted solvent molecules in the crystals of **7a** and **9b** were omitted using the SQUEEZE algorithm. The resulting new data sets were generated, and the structures were refined to convergence.[18] Selected bond distances and angles for all the compounds are given in the Supporting Information.

{η^5-[MeOC(O)]C_5H_4}Co{η^4-[MeOC(O)]C_4Ph_3} (1). $Co(PPh_3)_3Cl$ (8.80 g, 10.00 mmol) was added to a solution of Na{[MeOC(O)]-C_5H_4} (1.75 g, 12.00 mmol) in 10 mL of THF, and the mixture was stirred for 5 min. To this was added methyl 3-phenyl-2-propynoate (1.60 g, 10.00 mmol) in 100 mL of toluene, and the mixture was stirred for 40 min. To the resultant solution was added diphenylacetylene (1.78 g, 10.00 mmol), and the mixture was refluxed for 5 h. The reaction mixture was cooled, the solvent was evaporated off, and the residue was chromatographed on a neutral alumina

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column. Triphenylphosphine was removed by eluting the column with hexane. When the polarity was gradually increased (10% ethyl acetate−90% hexane) {η^5-[MeOC(O)]C_5H_4}Co(C_4Ph_4) was eluted followed by a third fraction, which on evaporation of the solvent gave a yellow crystalline powder characterized as {η^5-[MeOC(O)]C_5H_4}Co-{η^4-[MeOC(O)]C_4Ph_3} (**1**). Yield: 3.64 g, 7.00 mmol, 70%. Mp: 98−100 °C. Anal. Found: C, 71.50; H, 4.90. Calcd for $C_{31}H_{25}O_4Co$: C, 71.54; H, 4.84. IR (ν, cm^{-1}): 1708 vs (C═O). ^1H NMR (δ, 300 MHz, $CDCl_3$): 3.37 [3H, s, C(O)OCH_3], 3.83 [3H, s, C(O)OCH_3], 4.84 (2H, s, CpH), 5.27 (2H, s, CpH), 7.22−7.66 (15H, m, PhH); ^{13}C NMR (δ, 75 MHz, $CDCl_3$): 51.35−51.53 [C(O)OCH_3], 56.89, 79.66, 80.71 (C_4Cb), 84.25, 86.17, 86.84 (CpC), 127.18−133.47 (PhC), 165.90, 171.85 C(O). HRMS: calcd for $C_{31}H_{25}O_4CoNa$ 543.0977, found 543.0969.

[η^5-(COOH)C_5H_4]Co[η^4-(COOH)C_4Ph_3] (2). Potassium hydroxide (1.12 g, 20.00 mmol) dissolved in 8 mL of water was mixed with **1** (1.00 g, 1.92 mmol) in 100 mL of ethyl alcohol, and the mixture was refluxed for 30 h. The reaction was quenched with 2 M HCl (50 mL). After extraction with CH_2Cl_2 (100 mL), the organic phase was washed with 100 mL of 2 M aqueous HCl, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure to give a yellow solid which was identified as **2.** Yield: 0.90 g, 1.83 mmol, 96%. Mp: 226−228 °C. Anal. Found: C, 70.60; H, 4.40. Calcd for $C_{29}H_{21}O_4Co$: C, 70.74; H, 4.30. IR (ν, cm^{-1}): 1669 vs (C═O). ^1H NMR (δ, 300 MHz, d_6-DMSO): 4.84 (2H, s, CpH), 5.16 (2H, s, CpH), 7.20−7.59 (15H, m, PhH); ^{13}C NMR (δ, 75 MHz, d_6-DMSO): 58.47, 80.31, 81.24 (C_4Cb), 85.00, 87.39, 88.72 (CpC), 128.20−134.67 (PhC), 167.75, 173.17 C(O). HRMS: calcd for $C_{29}H_{21}O_4CoNa$ 515.0670, found 515.0645.

[η^5-(4-*i*Pr-2-Ox)C_5H_4]Co[η^4-(4-*i*Pr-2-Ox)C_4Ph_3] (3). Crude acid **2** (0.50 g, 1.02 mmol) was dissolved in CH_2Cl_2 (20 mL). Oxalyl chloride (0.28 g, 2.24 mmol) and DMF (1 drop) were added sequentially. Upon addition of the latter, gas evolution was observed. The resulting solution was stirred at room temperature. After 60 min, the solution was concentrated using a rotary evaporator. Excess oxalyl chloride and byproducts were removed by repeated extraction of the residue with CH_2Cl_2 (3 × 20 mL) to yield the acid chloride as a red-brown solid, which was used directly in the next step.

(*S*)-2-Amino-3-methyl-1-butanol (L-valinol; 0.21 g, 2.03 mmol) was taken up in a mixture of triethylamine (4 mL) and CH_2Cl_2 (15 mL). A solution of the crude acid chloride in 20 mL of CH_2Cl_2 was also transferred to this flask. The resulting solution was stirred at room temperature and, after 2 h, was cooled to 0 °C using an ice bath. Mesyl chloride (0.46 g, 4.00 mmol) was added, and the resulting solution was warmed to room temperature. After it was stirred for 16 h, the solution was washed with 30 mL of saturated aqueous sodium bicarbonate and 30 mL of brine using a separating funnel. The organic layer was dried over Na_2SO_4, filtered, and concentrated using a rotary evaporator. The residue was purified using a silica gel column with a 20% ethyl acetate−80% hexane mixture as eluent. Evaporation of the solvent gave **3** as a yellow viscous semisolid. Yield: 0.43 g, 0.69 mmol, 67%. $[\alpha]_D^{35}$ = −51.1° (c 0.20 in CH_2Cl_2). Anal. Found: C, 74.60; H, 6.10; N, 4.64. Calcd for $C_{39}H_{39}O_2N_2Co$: C, 74.75; H, 6.27; N, 4.47. IR (ν, cm^{-1}): 1648 vs (C═N). ^1H NMR (δ, 300 MHz, $CDCl_3$): 0.63−0.66 (3H, d, ^3J = 6.6 Hz, CHCH_3), 0.83−0.85(3H, d, ^3J = 6.0 Hz, CHCH_3), 0.89−0.91(3H, d, ^3J = 6.0 Hz, CHCH_3), 0.96−0.98(3H, d, ^3J = 6.0 Hz, CHCH_3), 1.46−1.52 [1H, m, CH(CH$_3$)$_2$], 1.84−1.86 [1H, m, CH(CH$_3$)$_2$], 3.34−3.39 (1H, m, CHCH$_2$), 3.45−3.66 (2H, m, CHCH_2), 3.81−3.89 (1H, m, CHCH$_2$), 3.96−4.23 (2H, m, CHCH_2), 4.63 (1H, s, CpH), 4.72 (1H, s, CpH), 5.03 (1H, s, CpH), 5.22 (1H, s, CpH), 7.05−7.71 (15H, m, PhH). ^{13}C NMR (δ, 75 MHz, $CDCl_3$): 18.13, 18.54, 18.76, 19.42, [CH(CH$_3$)$_2$], 32.64, 32.71 [CH(CH$_3$)$_2$], 58.27 (C_4Cb), 69.28, 69.58 (CHCH$_2$), 72.62, 73.00 (CHCH$_2$), 78.03, 79.72 (C_4Cb), 82.21, 83.72, 84.26, 85.42, 85.54 (CpC), 126.42−134.61 (PhC), 160.08, 164.02 (C═N), HRMS: calcd for $C_{39}H_{39}O_2N_2CoH$ 627.2722, found 627.2408.

Pd(OAc)[η^5-(4-*i*Pr-2-Ox)C_5H_4]Co[η^4-(4-*i*Pr-2-Ox)$C_4Ph_2(C_6H_4)$] (4). Palladium acetate (0.06 g, 0.27 mmol) was added to a solution of **3** (0.17 g, 0.27 mmol) in acetic acid (1.5 mL), and the mixture was stirred at room temperature for 5 min and then at 60 °C for 20 min. Acetic acid was removed under vacuum, and the resulting red mixture was dissolved first in 2 mL of dichloromethane followed by 5 mL of hexane, upon which a brown precipitate was found to form. The clear red solution was decanted to a conical flask, which upon standing for 2 h gave red crystals which were characterized as **4**. Yield: 0.16 g, 0.20 mmol, 76%. Mp: 174−176 °C dec. $[\alpha]_D^{35}$ = +160° (c 0.20 in CH_2Cl_2). Anal. Found: C, 62.12; H, 5.19; N, 3.65. Calcd for $C_{41}H_{41}O_4N_2Co$: C, 62.25; H, 5.22; N, 3.54. IR (ν, cm^{-1}): 1713, 1632. ^1H NMR (δ, 300 MHz, $CDCl_3$): 0.51−0.54 (3H, d, ^3J = 6.6 Hz, CHCH_3), 0.73−0.75 (3H, d, ^3J = 6.6 Hz, CHCH_3), 0.86−0.89 (3H, d, ^3J = 6.6 Hz, CHCH_3), 0.97−1.00 (3H, d, ^3J = 6.9 Hz, CHCH_3), 1.97 [1H, bs, CH(CH$_3$)$_2$], 2.02 [3H, bs, OC(O)CH_3], 2.46 [1H, bs, CH(CH$_3$)$_2$], 4.07−4.12 (2H, m, CHCH$_2$), 4.17−4.19 (4H, m, CHCH_2), 4.61 (2H, s, CpH), 5.04(2H, s, CpH), 6.65−7.47 (14H, m, PhH). ^{13}C NMR (75 MHz, $CDCl_3$): 15.21, 16.13, 17.77, 18.56 CHCH_3, 25.13 (OC(O)CH_3), 29.93, 30.84 [CH(CH$_3$)$_2$], 58.47(C_4Cb), 68.97, 69.36 (CHCH$_2$), 69.36, 71.13 (CHCH$_2$), 74.75, 79.66, 81. 50 (C_4Cb), 82.64, 85.70, 86.70, 87.83, 89.30 (CpC), 123.07, 124.76, 126.11, 127.31, 127.61, 128.31, 128.46, 129.46, 134.15, 134.83, 135.64, 136.27, 143.59 (PhC), 165.04, 168.65 (C═N), 177.25 (OCOCH$_3$). HRMS: calcd for $C_{39}H_{38}CoN_2O_2Pd$ 731.1300, found 731.1319.

Pd(Br)[η^5-(4-*i*Pr-2-Ox)C_5H_4]Co[η^4-(4-*i*Pr-2-Ox)$C_4Ph_2(C_6H_4)$] (5a). The palladacycle **4** (0.10 g, 0.13 mmol) was dissolved in 1 mL of acetone, and to this solution was added aqueous potassium bromide; the resulting mixture was stirred at room temperature overnight. The resulting precipitate was dissolved in dichloromethane (20 mL), and the solution was transferred to a separating funnel and washed with water (2 × 20 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated using a rotary evaporator. The orange powder obtained was characterized as **5a**. Yield: 0.09 g, 0.11 mmol, 86%. Mp: 178−179 °C dec. $[\alpha]_D^{35}$ = +175° (c 0.20 in CH_2Cl_2). ^1H NMR (δ, 300 MHz, $CDCl_3$): 0.54−0.57 (3H, d, ^3J = 6.9 Hz, CHCH_3), 0.64−0.67 (3H, d, ^3J = 6.9 Hz, CHCH_3), 0.87−0.89 (3H, d, ^3J = 6.6 Hz, CHCH_3), 1.05−1.08 (3H, d, ^3J = 6.9 Hz, CHCH_3), 1.71−1.79 [1H, m, CH(CH$_3$)$_2$], 2.28−2.57 [1H, m, CH(CH$_3$)$_2$], 3.87−4.00 (2H, m, CHCH$_2$), 4.07−4.55 (4H, m, CHCH_2), 4.63 (2H, s, CpH), 5.96 (2H, s, CpH), 6.66−8.01 (14H, m, PhH). ^{13}C NMR (δ, 75 MHz, $CDCl_3$): 15.99, 16.60, 17.46, 19.56 CHCH_3, 29.51, 30.92 [CH(CH$_3$)$_2$], 69.31, 69.51 (CHCH$_2$), 71.12, 71.47 (CHCH$_2$), 58.31, 74.70, 79.61, 79.93 (C_4Cb), 82.77, 85.82, 86.22, 87.26, 87.88 (CpC), 123.70−146.94 (PhC), 164.02, 167.97 (C═N).

Pd(I)[η^5-(4-*i*Pr-2-Ox)C_5H_4]Co[η^4-(4-*i*Pr-2-Ox)$C_4Ph_2(C_6H_4)$] (5b). The palladacycle **4** (0.11g, 0.14 mmol) was dissolved in 1 mL of acetone, and to this solution was added aqueous potassium iodide; the resulting mixture was stirred at room temperature overnight. The resulting precipitate was dissolved in dichloromethane (20 mL), transferred to a separating funnel, and washed with water (2 × 20 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated using a rotary evaporator. The concentrate was dissolved in a minimum amount of toluene, and this solution upon standing at room temperature gave red crystals characterized as **5b**. Yield: 0.11 g, 0.13 mmol, 92% Mp: 183−185 °C dec. $[\alpha]_D^{35}$ = +197° (c 0.20 in CH_2Cl_2). ^1H NMR (δ, 300 MHz, $CDCl_3$): 0.61−0.63 (3H, d, ^3J = 6.6 Hz, CHCH_3), 0.71−0.73 (3H, d, ^3J = 6.6 Hz, CHCH_3), 0.93−0.96 (3H, d, ^3J = 6.6 Hz, CHCH_3), 1.12−1.15 (3H, d, ^3J = 6.9 Hz, CHCH_3), 1.82−1.84 [1H, m, CH(CH$_3$)$_2$], 2.60−2.65 [1H, m, CH(CH$_3$)$_2$], 3.98−4.04 (2H, m, CHCH$_2$), 4.15−4.63 (4H, m, CHCH_2), 4.87 (2H, s, CpH), 5.03 (2H, s, CpH), 6.73−8.07 (14H, m, PhH). ^{13}C NMR (δ, 75 MHz, $CDCl_3$): 16.05, 16.67, 17.55, 19.65 CHCH_3, 29.57, 30.99 [CH-(CH$_3$)$_2$], 69.38, 69.56 (CHCH$_2$), 71.18, 71.54 (CHCH$_2$), 58.39, 74.74, 79.66, 80.00 (C_4Cb), 82.87, 85.89, 86.33, 87.33, 87.96 (CpC), 123.79−147.03 (PhC), 164.08, 168.02 (C═N).

{η^5-[MeC(O)]C_5H_4}Co{η^4-[MeOC(O)]C_4Ph_3} (6a). Using the same procedure utilized for the synthesis of **1**, compound **6a** was prepared by starting with Na{[MeC(O)]C_5H_4} (1.56 g, 12.00 mmol). The orange crystalline powder obtained was characterized as **6a**. Yield: 3.24 g, 6.43 mmol, 64%. Mp: 88−91 °C. Anal. Found: C, 73.60; H, 4.65. Calcd for $C_{31}H_{25}O_3Co$: C, 73.81; H, 5.00. IR (ν, cm^{-1}): 1703, 1670. ^1H NMR (δ, 300 MHz, $CDCl_3$): 1.79 [3H, s, C(O)CH_3], 3.86 [3H, s, C(O)OCH_3] 4.89 (2H, s, CpH), 5.24 (2H, s, CpH), 7.03−7.66 (15H,

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m, PhH). ^{13}C NMR (δ, 75 MHz, $CDCl_3$): 27.05 [C(O)CH_3], 51.61 [C(O)OCH_3], 57.31, 79.96, 81.00 (C_4Cb), 83.45, 87.27, 93.92 (CpC), 127.33−133.41 (PhC), 171.85 ($COOCH_3$), 196.74 ($COCH_3$). HRMS: calcd for $C_{31}H_{25}O_3CoNa$ 527.1033, found 527.1001.

[η^5-(Me)C_5H_4]Co{η^4-[MeOC(O)]C_4Ph_3} (6b). Using the same procedure utilized for the synthesis of **1**, compound **6b** was prepared by starting with Na[(Me)C_5H_4] (1.30 g, 12.74 mmol). The orange crystalline powder obtained was characterized as **6b**. Yield: 2.63 g, 5.52 mmol, 55%. Mp: 115−117 °C. Anal. Found: C, 75.60; H, 5.40. Calcd for $C_{30}H_{25}O_2Co$: C, 75.63; H, 5.29. IR (ν, cm^{-1}): 1710. ^{1}H NMR (δ, 300 MHz, $CDCl_3$): 1.70 (3H, s, CH_3), 4.49 (2H, s, CpH), 4.60 (2H, s, CpH), 7.05−7.68 (15H, m, PhH). ^{13}C NMR (δ, 75 MHz, $CDCl_3$): 10.83 (CH_3), 75.27, 78.53, 82.24 (C_4Cb), 82.27, 82.85, 93.78 (CpC), 125.83−132.62 (PhC), 171.76 ($COOCH_3$). HRMS: calcd for $C_{30}H_{25}O_2CoNa$ 499.1084, found 499.1078.

{η^5-[MeC(O)]C_5H_4}Co[η^4-(COOH)C_4Ph_3] (7a). Compound **6a** (1.00 g, 1.98 mmol) was converted to the corresponding acid **7a** by adopting the procedure used in the synthesis of **2**, which resulted in an orange powder. Yield: 0.95 g, 1.94 mmol, 98%. Mp: 158−160 °C. Anal. Found: C, 73.40; H, 4.70. Calcd for $C_{30}H_{23}O_3Co$: C, 73.47; H, 4.73. IR (ν, cm^{-1}): 1659. ^{1}H NMR (δ, 300 MHz, $CDCl_3$): 1.83 (3H, s, $COCH_3$), 4.98 (2H, s, CpH), 5.33 (2H, s, CpH), 7.28−7.71 (15H, m, PhH). ^{13}C NMR (δ, 75 MHz, $CDCl_3$): 27.32 ($COCH_3$) 80.85, 81.91 (C_4Cb), 83.72, 87.62, 94.24 (CpC), 127.66−133.32 (PhC), 177.11 (COOH), 197.10 ($COCH_3$). HRMS: calcd for $C_{30}H_{23}O_3CoNa$ 513.0877, found 513.0851.

[η^5-(Me)C_5H_4]Co[η^4-(COOH)C_4Ph_3] (7b). Compound **6b** (1.00g, 2.10 mmol) was converted to the corresponding acid **7b** by adopting the procedure used in the synthesis of **2**, which resulted in an orange powder. Yield: 0.91 g, 1.96 mmol, 94%. Mp: 197−199 °C. Anal. Found: C, 75.20; H, 4.93. Calcd for $C_{29}H_{23}O_2Co$: C, 75.32; H, 5.01. IR (ν, cm^{-1}): 1662. ^{1}H NMR (δ, 300 MHz, $CDCl_3$): 1.73 (3H, s, CH_3), 4.57 (2H, s, CpH), 4.69 (2H, s, CpH), 6.93−7.64 (15H, m, PhH). ^{13}C NMR (δ, 75 MHz, $CDCl_3$): 11.22 (CH_3) 77.36, 79.18, 83.51 (C_4Cb), 82.90, 83.94, 95.67 (CpC), 126−134 (PhC), 173.29 (COOH). HRMS: calcd for $C_{29}H_{23}O_2CoNa$ 485.0928, found 485.0930.

{η^5-[MeC(O)]C_5H_4}Co[η^4-(4-*i*Pr-2-Ox)C_4Ph_3] (8a). Using the procedure adopted for the synthesis of the bis(oxazoline) **3**, compound **8a** was prepared by starting with **7a** (0.50 g, 1.02 mmol). Compound **8a** was obtained as an orange viscous semisolid. Yield: 0.42 g, 0.75 mmol, 74%. $[\alpha]_D^{35}$ = −20.5° (*c* 0.20 in CH_2Cl_2). Anal. Found: C, 75.20; H, 5.85; N, 2.60. Calcd for $C_{35}H_{32}O_2N_1Co$: C, 75.39; H, 5.78; N, 2.51. IR (ν, cm^{-1}): 1626 vs (C═N). ^{1}H NMR (δ, 300 MHz, $CDCl_3$): 0.92−0.95 (3H, d, ^3J = 6.9 Hz, CHCH_3), 1.03−1.05(3H, d, ^3J = 6.9 Hz, CHCH_3), 1.65 [3H, s, C(O)CH_3], 1.76−1.82 [1H, m, CH(CH_3)$_2$], 3.85−3.93 (1H, m, CHCH$_2$), 4.01−4.06 (1H, m, CHCH_2), 4.29−4.35 (1H, m, CHCH_2), 4.77 (2H, s, CpH), 5.11 (1H, s, CpH), 5.16(1H, s, CpH), 7.08−7.66 (15H, m, PhH). ^{13}C NMR (δ, 75 MHz, $CDCl_3$): 18.93, 19.26 [CH(CH_3)$_2$], 27.15 ($COCH_3$), 33.03 [CH(CH_3)$_2$], 58.95 (C_4Cb), 70.22 ($CHCH_2$), 73.48 ($CHCH_2$), 78.05, 78.43, 80.46 (C_4Cb), 83.22, 83.43, 87.15, 87.17, 93.90 (CpC), 127.11−134.50 (PhC), 163.72 (C═N), 197.16 ($COCH_3$). HRMS: calcd for $C_{35}H_{32}O_2NCoH$ 558.1843, found 558.1818.

[η^5-(Me)C_5H_4]Co[η^4-(4-*i*Pr-2-Ox)C_4Ph_3] (8b). Using the procedure adopted for the synthesis of the bis(oxazoline) **3**, compound **8b** was prepared by starting with **7b** (0.50 g, 1.02 mmol). Compound **8b** was obtained as an orange viscous semisolid. Yield: 0.12 g, 0.23 mmol, 75%. $[\alpha]_D^{35}$ = −18.6° (*c* 0.20 in CH_2Cl_2). Anal. Found: C, 77.10; H, 6.20; N, 2.70. Calcd for $C_{34}H_{32}O_1N_1Co$: C, 77.11; H, 6.09; N, 2.64. IR (ν, cm^{-1}): 1627 vs (C═N). ^{1}H NMR (δ, 300 MHz, $CDCl_3$): 1.03−1.05 (3H, d, ^3J = 6.6 Hz, CHCH_3), 1.12−1.14 (3H, d, ^3J = 6.6 Hz, CHCH_3), 1.63 [3H, s, Cp(CH_3)], 1.81−1.91 [1H, m, CH(CH_3)$_2$], 3.96−4.03 (1H, m, CHCH$_2$), 4.09−4.14 (1H, m, CHCH_2), 4.34−4.40 (1H, m, CHCH_2), 4.53 (2H, s, CpH), 4.63 (2H, s, CpH), 7.21−7.79 (15H, m, PhH). ^{13}C NMR (δ, 75 MHz, $CDCl_3$): 11.55 [3H, s, Cp(CH_3)], 18.83, 19.16 [CH(CH_3)$_2$], 33.19 [CH(CH_3)$_2$], 57.13 (C_4Cb), 69.93 ($CHCH_2$), 73.09 ($CHCH_2$), 75.87, 78.88, 83.05 (C_4Cb), 82.41, 82.53, 83.42, 83.58, 95.36 (CpC), 126.23−135.86 (PhC), 164.98 (C═N). HRMS: calcd for $C_{34}H_{32}ONCoH$ 530.1894, found 530.1875.

Synthesis of Palladacycle 9a. Palladium acetate (0.07 g, 0.31 mmol) was added to a solution of **8a** (0.12 g, 0.21 mmol) in acetic acid (1 mL). The red solution was stirred at room temperature and then heated to 60 °C. An orange precipitate was found to form as the reaction proceeded. The solution was cooled to room temperature, and the precipitate was filtered and washed with glacial acetic acid. The orange compound obtained was characterized as **9a**. Yield: 0.12 g, 0.07 mmol, 66%. Mp: 180−183 °C dec. $[\alpha]_D^{35}$ = −30.6° (*c* 0.20 in CH_2Cl_2). Anal. Found: C, 56.05; H, 4.39; N, 1.69. Calcd for $C_{78}H_{74}Co_2N_2O_{12}Pd_3$: C, 56.15; H, 4.47; N, 1.68. IR (ν, cm^{-1}): 1630 vs (C═N), 1573. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.25−0.27 (3H, d, ^3J = 6.6 Hz, CHCH_3), 0.75−0.77 (3H, d, ^3J = 6.9 Hz, CHCH_3), 1.87 [6H, s, C(O)CH_3], 1.91 (12H, s, OC(O)CH_3), 3.22 [2H, bs, CH(CH_3)$_2$], 4.42−4.46 (2H, m, CHCH$_2$), 4.61−4.65 (4H, m, CHCH_2), 5.54 (2H, s, CpH), 5.78 (2H, s, CpH), 6.19 (2H, s, CpH), 6.28 (2H, s, CpH), 6.62−7.78 (28H, m, PhH). ^{13}C NMR (δ, 75 MHz, $CDCl_3$): 13.05, 17.46, 22.61, 22.67 [CH(CH_3)$_2$], 26.37 [Cp($COCH_3$)], 28.49 [CH(CH_3)], 53.27 (C_4Cb), 69.12 ($CHCH_2$), 69.77 ($CHCH_2$), 74.69, 78.92, 81.11 (C_4Cb), 84.30, 84.89, 89.09, 90.40, 94.45 (CpC), 120.83, 122.15, 124.86, 125.15, 126.28, 126.74, 127.00, 127.46, 127.62, 128.04, 128.89 (PhC), 169.06 (C═N), 182.66, 184.04 ($COCH_3$), 197.48 [Cp($COCH_3$)].

Synthesis of Palladacycle 9b. Palladium acetate (0.14 g, 0.62 mmol) was added to a solution of **8b** (0.22 g, 0.41 mmol) in acetic acid (1 mL). The red solution was stirred at room temperature and then heated to 60 °C. An orange precipitate was found to form as the reaction proceeded. The solution was cooled to room temperature, and the precipitate was filtered and washed with glacial acetic acid. The orange compound obtained was characterized as **9b**: Yield: 0.23 g, 0.14 mmol, 69%. Mp: 185−188 °C dec. $[\alpha]_D^{35}$ = −26.5° (*c* 0.20 in CH_2Cl_2). Anal. Found: C, 56.45; H, 4.65; N, 1.89. Calcd for $C_{76}H_{74}Co_2N_2O_{10}Pd_3$: C, 56.61; H, 4.63; N, 1.74. IR (ν, cm^{-1}): 1625 vs (C═N), 1574. ^{1}H NMR (δ, 300 MHz, $CDCl_3$): 0.25−0.27 (3H, ^3J = 6.6 Hz, CHCH_3), 0.75−0.77 (3H, d, ^3J = 6.9 Hz, CHCH_3), 1.65 [6H, s, Cp(CH_3)], 1.89 (12H, s, OC(O)CH_3), 3.30 [2H, bs, CH(CH_3)$_2$], 4.44 (2H, s, CHCH$_2$), 4.59−4.65 (4H, m, CHCH_2), 4.79 (2H, s, CpH), 5.36 (2H, s, CpH), 5.55 (2H, s, CpH), 5.94 (2H, s, CpH), 6.62−7.86 (28H, m, PhH). ^{13}C NMR (75 MHz, $CDCl_3$): 11.58 Cp(CH_3), 13.98, 18.51 [CH(CH_3)$_2$], 23.53, 23.76 $COCH_3$, 29.50 [CH(CH_3)], 53.18 (C_4Cb), 68.95 ($CHCH_2$), 69.77 ($CHCH_2$), 71.80, 79.99 (C_4Cb), 84.71, 85.26, 85.39, (CpC), 122.84, 125.17, 125.76, 126.19, 126.93, 127.76, 128.24, 128.30, 130.06, 135.74, 136.45, 138.21, 138.25 (PhC), 169.80 (C═N), 182.54, 184.13 ($COCH_3$).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables, figures, and CIF files giving selected bond lengths and angles and crystallographic data for compounds **2**, **4**, **5b**, **7a**, and **9b**, X-ray crystal structures of compounds **2** and **7a**, and ^{1}H and ^{13}C NMR spectra of compounds **4** and **9a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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