temperature for 30 min. The AgBr formed was filtered off; the yellow solution was evaporated to dryness; and the residue was washed with 10 mL of *n*-hexane. Complex 1, in 73% yield, was obtained.

Reaction of $(NBu_4)_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ with $O_3ClOAgPPh_3$. To a solution of 0.100 g (0.0532 mmol) of $(NBu_4)[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ (1) in 15 mL of CH_2Cl_2 at −30 °C was added 0.025 g (0.053 mmol) of $O_3ClOAgPPh_3$; the mixture was stirred for 30 min at this temperature. The solution was pumped to dryness (−30 °C), and the residue was treated with 20 mL of $O(C_2H_5)_2$ (−30 °C). After separation of the insoluble NBu_4ClO_4, the solution was evaporated to dryness, and 10 mL of *n*-hexane was added. Complex 3 (69% yield) was obtained.

Preparation of Crystals for X-ray Structure Determination. Crystals of $(NBu_4)_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ (1) and of $(NBu_4)[Pt_2Ag(\mu\text{-}C_6F_5)_2(C_6F_5)_4 \cdot O(C_2H_5)_2]$ (2) were obtained by slow diffusion at −30 °C of *n*-hexane into dichloromethane solutions of the corresponding complexes.

Crystal Structure Analyses. Routine procedures were used for the collection of X-ray diffraction dat[18] from crystals of $(NBu_4)_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]\cdot H_2O$ (1) and $(NBu_4)[Pt_2Ag(\mu\text{-}C_6F_5)_2(C_6F_5)_4 \cdot O(C_2H_5)_2$ (2). A crystal of 1 was mounted on a glass fiber and covered with epoxy; the specimen of compound 2 was sealed inside a capillary tube. The lattice dimensions and Laue group of each crystal were verified by normal-beam oscillation photography; these and other important crystal and experimental parameters are given in Table II.

Absorption corrections were applied to both data sets, based in each case on azimuthal scans of several reflections.[19] In addition, the data for compound 2 were corrected for decay, since the intensities of three monitor reflections dropped by an average of 24.5% during the course of 200 h of X-ray exposure.

The structure of 1 was solved by direct methods and developed and refined routinely.[20] No hydrogen atoms were included in the model. All non-hydrogen atoms were refined with anisotropic displacement parameters. In the final, convergent refinement, 465 parameters were fitted to 3671 data, for a data-to-parameter ratio of 7.9. The least-squares residuals are summarized in Table II.

The heavy atoms in the structure of 2 were located by direct methods, and the structure was developed and refined in a sequence of difference Fourier maps and least-squares calculations. During the late stages of refinement, the two terminal carbon atoms of the diethyl ether moiety ligated to silver showed signs of indeterminacy under normal least-squares analysis. Loose geometrical restraints were used for the C_α–C_β distances, in order to impose chemical sense on the dimensions of this group. In addition, a free *n*-hexane molecule was located on a crystallographic inversion center. Three unique atomic sites were identified which, along with their three symmetry congeners, formed a chain pattern which we modeled as one molecule of *n*-C_6H_{14}. The whole set of three unique sites was given an overall isotropic displacement parameter. The parameters of this group, like those of the carbon atoms of the ligated diethyl ether, were not allowed to vary in the final, unconditional structure-factor least-squares refinement.

In the final refinement, 779 variable parameters were fitted to 4061 data, for a data-to-parameter ratio of 5.2. The refinement converged with residuals given in Table II. There was no significant correlation in the least-squares analysis; and listings of residuals as functions of $(\sin \theta)/\lambda$, $|F_o|$, and indices revealed no systematic trends in the error function.

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Registry No. 1, 116349-58-7; $1\cdot H_2O$, 116323-87-6; 2, 95674-06-9; $2\cdot O(C_2H_5)_2\cdot {}^1/_2 n\text{-}C_6H_{14}$, 116323-90-1; 3, 116349-60-1; 4, 116323-82-1; 5, 66302-90-7; 6, 116323-84-3; $(NBu_4)_2[Pt(C_6F_5)_3Cl]$, 90621-02-6; Ag, 7440-22-4; Pt, 7440-06-4.

Supplementary Material Available: Complete lists of bond distances, bond angles, and anisotropic displacement parameters for the crystal structures of compounds 1 and 2 (14 pages); structure factor tables for 1 and 2 (40 pages). Ordering information can be found on any current masthead page.

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Preparation of Phenylplatinum–Zirconium Complexes with $Ph_2PC_5H_4$ or $PhP(C_5H_4)_2$ Bridging Ligands and Their Reactions with Carbon Monoxide

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Reaction of $[PtPh_2(cod)]$ or $[PtClPh(cod)]$ with $(Ph_2PC_5H_4)_2ZrCl_2$ yields the $Ph_2PC_5H_4$-bridged species $[PtXPh(Ph_2PC_5H_4)_2ZrCl_2]$ (X = Ph, Cl). Treatment of $[PtPh_2(cod)]$ or $[PtClPh(cod)]$ with 2 equiv of $PhP(C_5H_4)_2ZrCl_2$, prepared by reaction of $[ZrCl_4(THF)_2]$ with $(TlC_5H_4)_2PPh$, yields *cis*-$[PtPh_2\{PhP(C_5H_4)_2ZrCl_2\}_2]$ or *trans*-$[PtClPh\{PhP(C_5H_4)_2ZrCl_2\}_2]$. Each of the mixed-metal complexes has been isolated as an air-sensitive solid and characterized by elemental analysis and NMR spectroscopy. $[PtPh_2(Ph_2PC_5H_4)_2ZrCl_2]$ does not react with carbon monoxide, and *cis*-$[PtPh_2\{PhP(C_5H_4)_2ZrCl_2\}_2]$ undergoes a slow displacement of phosphine by CO, whereas the two chlorophenylplatinum complexes undergo smooth carbonylation to the corresponding benzoylplatinum species.

Introduction

Mixed-metal complexes in which the two metal centers are held in close proximity to one another have received considerable attention recently. Complexes suitable for the activation of small, polar molecules, such as carbon monoxide, should contain two widely different metals, yet few species containing a d^0 metal and a d^8 or d^{10} metal have been prepared. For those that have been formed, most have involved synthesis of an organometallic complex with one or two pendant phosphine groups, followed by coordination of these groups to a suitable late-transition-metal complex.[1-3] In addition, $[Cp_2Zr(PPh_2)_2]$ has been em-

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Table I. NMR Spectroscopic Parameters for the Zirconium and Zirconium–Platinum Complexes[a]

complex	^{1}H NMR	^{13}C{^{1}H} NMR	^{31}P{^{1}H} NMR
$(Ph_2PC_5H_4)_2ZrCl_2$	6.12 (m, 4 H), 6.15 (m, 4 H), 7.04–7.16 (m, 20 H)	118.28 (br s, C_γ), 122.12 (d, $^2J_{PC}$ = 10.5 Hz, C_β), 125.12 (d, $^1J_{PC}$ = 17.0 Hz, C_α), 128.54 (d, $^3J_{PC}$ = 6.7 Hz, C_3), 129.28 (s, C_4), 133.89 (d, $^2J_{PC}$ = 19.6 Hz, C_2), 136.76 (d, $^1J_{PC}$ = 12.6 Hz, C_1)	−17.2
$PhP(C_5H_4)_2ZrCl_2$	6.06 (m, 2 H, H_γ), 6.29 (m, 2 H, H_β), 6.80 (m, 2 H, H'_β), 6.98 (m, 2 H, H'_γ), 7.49 (m, 3 H), 7.72 (m, 2 H)	104.21 (d, $^1J_{PC}$ = 27.3 Hz, C_α), 110.82 (d, $^3J_{PC}$ = 6.6 Hz, C_γ), 117.83 (d, $^2J_{PC}$ = 36.8 Hz, C_β), 123.01 (d, $^2J_{PC}$ = 9.5 Hz, C'_β), 128.94 (s, C_4), 129.08 (d, $^3J_{PC}$ = 4.5 Hz, C_3), 130.81 (s, C'_γ), 130.83 (d, $^2J_{PC}$ = 14.0 Hz, C_2), 133.65 (d, $^1J_{PC}$ = 7.1 Hz, C_1)	−28.9
$PtPh_2(Ph_2PC_5H_4)_2ZrCl_2$	6.38 (m, 4 H), 6.63 (m, 4 H, Cp), 6.80 (m, 4 H, Cp), 6.85 (m, 2 H), 7.22–7.39 (m, 24 H)[b]	118.39 (d, $^1J_{PC}$ = 36.6 Hz, C_α), 119.27 (t, J_{PC} = 4.3 Hz, C_β), 120.60 (s, $^4J_{PtC}$ = 9.0 Hz, PtC_4), 126.04 (br s, C_γ), 126.90 (s, $^3J_{PtC}$ = 67.4 Hz, PtC_3), 127.99 (t, J_{PC} = 5.0 Hz, C_3), 130.20 (s, C_4), 132.42 (dd, $^1J_{PC}$ = 54.6 Hz, $^3J_{PC}$ = 2.7 Hz, C_1) 134.02 (t, $^2J_{PC}$ = 5.5 Hz, C_2), 135.81 (s, $^2J_{PtC}$ = 30.5 Hz, PtC_2), 159.87 (dd, $^2J_{PC}$ = 111.3 Hz (trans), 13.2 Hz (cis), $^1J_{PtC}$ not observed, PtC_1)	13.5 ($^1J_{PtP}$ = 1750 Hz)
$PtClPh(Ph_2PC_5H_4)_2ZrCl_2$	5.83 (m, 2 H, Cp), 6.50 (m, 2 H), 6.58 (m, 2 H, Cp), 6.99–7.80 (m, 23 H), 7.17 (m, 4 H, Cp)[b]	116.03 (d, J_{PC} = 35.7 Hz), 117.62 (d, J_{PC} = 57.0 Hz), 120.07 (d, J_{PC} = 9.0 Hz, J_{PtC} = 34.2 Hz), 121.18 (d, J_{PC} = 5.0 Hz), 122.35 (s), 124.58 (br s), 126.94 (d, J_{PC} = 8.0 Hz), 127.68 (d, J_{PC} = 8.0 Hz), 128.16 (d, J_{PC} = 11.1 Hz), 128.46 (d, J_{PC} = 10.1 Hz), 131.0 (br m), 134.06 (d, J_{PC} = 11.1 Hz, J_{PtC} = 31.7 Hz), 135.13 (d, J_{PC} = 11.1 Hz), 135.20 (s)	13.2 (d, $^2J_{PP}$ = 17 Hz, $^1J_{PtP}$ = 1523 Hz, P trans to Ph), 12.1 (d, $^2J_{PP}$ = 17 Hz, $^1J_{PtP}$ = 4428 Hz, P trans to Cl)
cis-$PtPh_2\{PhP(C_5H_4)_2ZrCl_2\}_2$	5.68 (m, 4 H), 5.73 (m, 4 H), 5.78 (m, 4 H), 5.83 (m, 4 H), 6.85–7.80 (m, 20 H)[b]		−1.7 ($^1J_{PtP}$ = 1725 Hz)
trans-$PtClPh\{PhP(C_5H_4)_2ZrCl_2\}_2$	5.82 (m, 4 H), 6.45 (m, 4 H), 6.82 (m, 4 H), 6.88 (m, 4 H), 7.00–7.95 (m, 15 H)[b]		5.2 ($^1J_{PtP}$ = 3247 Hz)

[a] In $CDCl_3$ solution. Chemical shifts in δ. Assignments are as follows: α, β, and γ refer to Cp ring; C_1–C_4 refer to Ph attached to P; PtC_1–PtC_4 refer to Ph attached to Pt. [b] In CD_2Cl_2 solution.

ployed to form bridging phosphido species with nickel(0), palladium(0), or platinum(0),[4] whereas $[Cp_2Hf(PR_2)_2]$ species have been attached to nickel(0) or rhodium(I).[5] Titanium–copper complexes with bridging thiolate or phosphinoalkanethiolate ligands have also been prepared.[6] A quite different synthetic strategy has been used in the reaction of $[(C_5Me_5)Zr(CH_3)_3]$ with $[Ni(Ph_2PCH_2OH)_4]$, which proceeds by methane elimination to yield $[(C_5Me_5)Zr(\mu\text{-}OCH_2PPh_2)_3NiL]$.[7]

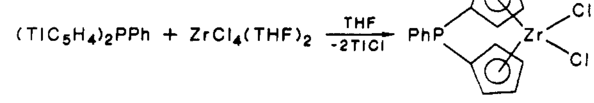
Although phosphido-bridged Zr(IV)–Pt(0) complexes have been prepared,[4] no Zr(IV)–Pt(II) complexes had been reported prior to this work. Herein we report the synthesis of a series of phenylplatinum(II) species linked to Zr(IV) by means of $Ph_2PC_5H_4$ or $PhP(C_5H_4)_2$ bridges and the reactions of these complexes with carbon monoxide. A preliminary account of part of this work has appeared.[8]

Results and Discussion

We have prepared (diphenylphosphino)cyclopentadienylthallium (δ(P) −16.7 in DMSO-d_6) according to the method of Rausch[9] and generated the related compound $(TlC_5H_4)_2PPh$ by the sequence shown in eq 1. (The

$$2C_5H_5Tl + Cl_2PPh \xrightarrow[-2TlCl]{Et_2O} (C_5H_5)_2PPh \xrightarrow[-2EtOH]{2TlOEt} (TlC_5H_4)_2PPh \quad (1)$$

latter is too insoluble to obtain its NMR spectrum.) Each thallium compound reacts with $[ZrCl_4(THF)_2]$. Thus we have used $TlC_5H_4PPh_2$ in a modified synthesis of $[(Ph_2PC_5H_4)_2ZrCl_2]$[10] and prepared the novel complex $[PhP(C_5H_4)_2ZrCl_2]$, which is isolated as a light yellow, air-sensitive solid, according to eq 2. NMR characteri-



(2)

zation of the zirconium complexes is given in Table I. The spectra for $[(Ph_2PC_5H_4)_2ZrCl_2]$ are unremarkable, exhibiting a single ^{31}P resonance and the expected number of ^{13}C signals for a compound in which all the phenyl groups, and the two C_5H_4 moieties, are magnetically equivalent.

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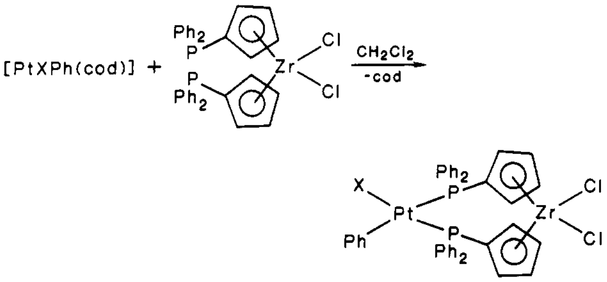
Table II. $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR Spectra of the Products of the Reactions of the Zr-Pt Complexes with ^{13}CO[a]

complex	$^{13}C\{^1H\}$ NMR δ	$^{31}P\{^1H\}$ NMR δ
$PtCl(COPh)(Ph_2PC_5H_4)_2ZrCl_2$	226.3 (d, $^2J_{PC}$ = 122 Hz, $^1J_{PtC}$ = 740 Hz)	6.3 (dd, $^2J_{PC}$ = 4 Hz, $^2J_{PP}$ = 21 Hz, $^1J_{PtP}$ = 4720 Hz, P trans to Cl), 9.3 (dd, $^2J_{PC}$ = 122 Hz, $^2J_{PP}$ = 21 Hz, $^1J_{PtP}$ = 1395 Hz, P trans to COPh)
trans-$PtCl(COPh)\{PhP(C_5H_4)_2ZrCl_2\}_2$	209.3 (t, $^2J_{PC}$ = 6 Hz, $^1J_{PtC}$ = 931 Hz)	1.7 (d, $^2J_{PC}$ = 6 Hz, $^1J_{PtP}$ = 3502 Hz)
cis-$PtPh_2(CO)\{PhP(C_5H_4)_2ZrCl_2\}$	180.0 (d, $^2J_{PC}$ = 5 Hz, $^1J_{PtC}$ = 971 Hz)	0.3 (d, $^2J_{PC}$ = 5 Hz, $^1J_{PtP}$ = 1527 Hz)

[a] In $CDCl_3$ solution.

However, the C_5H_4 units in $[PhP(C_5H_4)_2ZrCl_2]$ give rise to four ^1H and five ^{13}C resonances. Assignments of the ^{13}C resonances to C_5H_4 or Ph rings were made from the ^{13}C–^1H shift-correlated (HETCOR) 2D spectrum, and the ^1H resonances for the C_5H_4 unit were assigned by using the ^1H–^1H shift-correlated (COSY) 2D spectrum. The two C_5H_4 rings are identical, but all five ring positions are rendered magnetically nonequivalent by the presence of the sp^3-hybridized phosphorus atom bearing a lone pair and a phenyl group. Similar spectroscopic observations have been made for [1]ferrocenophanes, including $[Fe(C_5H_4)_2PPh]$.[11]

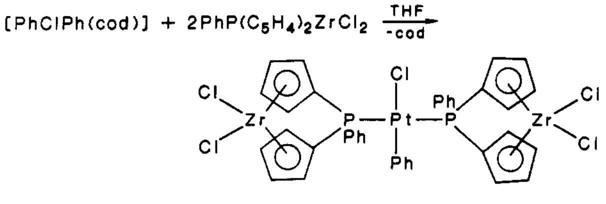
Reaction of $[(Ph_2PC_5H_4)_2ZrCl_2]$ with $[PtPh_2(cod)]$ or $[PtClPh(cod)]$ in CH_2Cl_2 solution results in displacement of cyclooctadiene by the phosphino groups (eq 3). In each case the product is of cis geometry at platinum, as evidenced by the small value of $^1J_{PtP}$ in the diphenyl complex and the nonequivalence of the phosphorus atoms in $[PtClPh(Ph_2PC_5H_4)_2ZrCl_2]$. Complete assignment of the $^{13}C\{^1H\}$ NMR spectrum is possible for $[PtPh_2(Ph_2PC_5H_4)_2ZrCl_2]$, which contains a plane of symmetry, but the complexity of the spectrum for $[PtClPh(Ph_2PC_5H_4)_2ZrCl_2]$ has prevented unambiguous assignment of all the ^{13}C resonances (Table I). As an alternative route to $[PtPh_2(Ph_2PC_5H_4)_2ZrCl_2]$, we have found that $[PtPh_2(cod)]$ reacts with 2 equiv of $TlC_5H_4PPh_2$ to give *cis*-$[PtPh_2(Ph_2PC_5H_4Tl)_2]$ [δ(P) 10.4 ($^1J_{PtP}$ 1840 Hz) in DMSO-d_6], which then reacts cleanly with $[ZrCl_4(THF)_2]$ to yield the desired product. Thus, the mixed-metal complex may be constructed in either of two ways.



(3)

X = Ph, Cl

When $[PtClPh(cod)]$ is added to a THF solution containing 2 equiv of $[PhP(C_5H_4)_2ZrCl_2]$, a complex of trans geometry at platinum is obtained (eq 4). The trans geometry follows from the equivalence of the phosphorus atoms, and the value of $^1J_{PtP}$ (Table I) is typical of a complex of the type *trans*-$[PtClPh(PR_3)_2]$.[12] When $[PtPh_2(cod)]$ is treated analogously, however, *cis*-$[PtPh_2\{PhP(C_5H_4)_2ZrCl_2\}_2]$ is obtained, the small value of $^1J_{PtP}$ being indicative of a phosphorus atom lying trans to Ph. The low solubility of each of these complexes prevented us from obtaining satisfactory $^{13}C\{^1H\}$ NMR spectra, but four ^1H signals are observed for the Cp rings in each case. The diphenyl complex is converted slowly to *trans*-$[PtClPh\{PhP(C_5H_4)_2ZrCl_2\}_2]$ in $CDCl_3$ solution; the reaction is 40% complete after 7 days at ambient temperature and is virtually quantitative after 48 h at 55 °C. It seemed reasonable to conclude that this proceeds by reaction with the solvent, but conversion also occurs in C_6D_6 where cleavage of the Zr–Cl bonds must occur. It may be that Cl for Ph exchange between platinum and zirconium takes place here, but the low solubilities of the complexes in this solvent have precluded identification of any Zr–Ph species.



(4)

We have studied the reactions of the Zr–Pt complexes with carbon monoxide in $CDCl_3$ solution, using ^{13}CO to facilitate monitoring the reactions by $^{13}C\{^1H\}$ NMR spectroscopy. No reaction of $[PtPh_2(Ph_2PC_5H_4)_2ZrCl_2]$ with CO occurs after 7 days at ambient temperature. However, with $[PtClPh(Ph_2PC_5H_4)_2ZrCl_2]$ reaction is complete within 3 days. The major product is identified as $[PtCl(COPh)(Ph_2PC_5H_4)_2ZrCl_2]$ (Table II), but a minor species is also observed at δ(C) 212.68 (t, $^2J_{PC}$ = 6 Hz, $^1J_{PtC}$ = 1014 Hz) to which we tentatively assign the dimeric structure *trans,trans*-$[PtCl(COPh)\{\mu\text{-}(Ph_2PC_5H_4)_2ZrCl_2\}]_2$. We note that in the reaction of $[PtClPh(dppp)]$ (dppp = 1,3-bis(diphenylphosphino)propane) with CO the major product is $[PtCl(COPh)(dppp)]$ [δ(C) 253.83 (dd $^2J_{PC}$ = 125, 4 Hz, $^1J_{PtC}$ = 766 Hz); δ(P) −8.5 (dd, $^2J_{PC}$ = 126 Hz, $^2J_{PP}$ = 29 Hz, $^1J_{PtP}$ = 1402 Hz) and δ(P) −5.3 (d, $^2J_{PP}$ = 29 Hz, $^1J_{PtP}$ = 4283 Hz)], but a minor species is found at δ(C) 211.63 (t, $^2J_{PC}$ = 5 Hz, $^1J_{PtC}$ = 1009 Hz). When $[PtCl(COPh)(cod)]$ is treated with $[(Ph_2PC_5H_4)_2ZrCl_2]$ in $CDCl_3$ solution, only the monomeric product is detected.

When a $CDCl_3$ solution of *cis*-$[PtPh_2\{PhP(C_5H_4)_2ZrCl_2\}_2]$ is treated with CO for 3 days, about 60% of the starting material remains. The partial reaction involves phosphine displacement by CO to give *cis*-$[PtPh_2(CO)\{PhP(C_5H_4)_2ZrCl_2\}]$ (Table II) and free $PhP(C_5H_4)_2ZrCl_2$ (δ(P) −28.9). A similar reaction has been observed for *cis*-$[PtPh_2(PPh_3)_2]$.[13] The reaction of *trans*-$[PtClPh\{PhP(C_5H_4)_2ZrCl_2\}_2]$ with CO is 50% complete after 24 h, the only product being *trans*-$[PtCl(COPh)\{PhP(C_5H_4)_2ZrCl_2\}_2]$ (Table II); the same product is generated quantitatively by addition of 2 equiv of $PhP(C_5H_4)_2ZrCl_2$ to a $CDCl_3$ solution of $[PtCl(COPh)(cod)]$.

Thus, we have demonstrated that we can construct Zr(IV)–Pt(II) complexes containing $Ph_2PC_5H_4$ or $PhP(C_5H_4)_2$ bridging units. In the former case, we have shown that the same complex is obtained if the bridging ligand is first attached to zirconium or to platinum. The complexes $[PtClPh(Ph_2PC_5H_4)_2ZrCl_2]$ and *trans*-$[PtClPh\{PhP(C_5H_4)_2ZrCl_2\}_2]$ each react with carbon monoxide to give

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the corresponding benzoyl species, but the reactions occur at rates similar to those for [PtClPh(dppp)] and *trans*-[PtClPh(PPh_3)$_2$], respectively, indicating that the presence of the zirconium center has little or no effect on the rates of carbonylation.

Experimental Section

NMR spectra were recorded on a Varian XL-300 spectrometer operating in the Fourier transform mode. ^{1}H and ^{13}C chemical shifts are relative to tetramethylsilane, and ^{31}P shifts are relative to external H_3PO_4, positive shifts representing deshielding. Microanalyses were performed by Galbraith Microanalytical Laboratories, Knoxville, TN.

Chlorodiphenylphosphine and dichlorophenylphosphine were obtained from Aldrich and Alfa respectively, and used as received. Carbon-13 monoxide (99% labeled) was purchased from Aldrich. The compounds [$ZrCl_4(THF)_2$],[14] $TlC_5H_4PPh_2$,[9] [PtClPh(cod)],[15] [$PtPh_2$(cod)],[15] and [PtCl(^{13}COPh)(cod)][16] were prepared by established methods.

All manipulations were carried out under an atmosphere of dry argon in a Vacuum Atmospheres glovebox using standard Schlenk techniques. Hexane, pentane, ether, toluene, THF, and petroleum ether were distilled from sodium benzophenone ketyl. Dichloromethane and chloroform were distilled from P_2O_5 and degassed thoroughly before use.

Preparation of (TlC_5H_4)$_2$PPh. Dichlorophenylphosphine (4.48 g, 25.0 mmol) was added slowly to a stirred suspension of TlC_5H_5 (13.5 g, 50.1 mmol) in ether (100 mL). After 1 h the precipitated TlCl was removed by filtration, and thallium ethoxide (12.5 g, 50.1 mmol) was added dropwise to the filtrate, immediately producing a yellow precipitate. After 2 h the mother liquor was decanted, and the product was washed with several portions of ether and dried in vacuo (10.1 g, 63%).

Preparation of ($Ph_2PC_5H_4$)$_2$ZrCl$_2$.[10] Thallium (diphenylphosphino)cyclopentadienide (3.37 g, 7.43 mmol) and bis(tetrahydrofuran)tetrachlorozirconium (1.40 g, 3.71 mmol) were mixed in a 100-mL round-bottomed flask. Toluene (25 mL) was added, and the mixture was stirred overnight and then filtered through a glass frit. The TlCl was washed with two 5-mL portions of toluene, and the combined pale orange solution was evaporated to dryness. The residue was washed with four 10-mL portions of hexane, leaving the product as a light tan solid in ca. 75% yield. Recrystallization from toluene/petroleum ether produced yellow needles. Anal. Calcd for $C_{34}H_{28}Cl_2P_2Zr$: C, 61.81; H, 4.27. Found: C, 60.61; H, 4.19.

Preparation of PhP(C_5H_4)$_2$ZrCl$_2$. Tetrahydrofuran (100 mL) was added to a flask containing (TlC_5H_4)$_2$PPh (5.86 g, 9.09 mmol) and [$ZrCl_4(THF)_2$] (3.43 g, 9.09 mmol). The mixture was stirred at room temperature overnight and then filtered through a glass frit. The TlCl was washed with two 5-mL portions of tetrahydrofuran, and the pale orange solution was evaporated to dryness. The residue was washed with pentane (10 mL), leaving PhP(C_5H_4)$_2$ZrCl$_2$ as a light yellow powder (3.10 g, 86%). Anal. Calcd for $C_{16}H_{13}Cl_2PZr$: C, 48.24; H, 3.29. Found: C, 48.13; H, 4.15.

Preparation of *cis*-[$PtPh_2$($Ph_2PC_5H_4Tl$)$_2$]. To a solution of [$PtPh_2$(cod)] (0.15 g, 0.33 mmol) in tetrahydrofuran (25 mL) was added $TlC_5H_4PPh_2$ (0.30 g, 0.66 mmol) in small portions. After 3 h the yellow precipitate was filtered, washed with three 5-mL portions of ether, and dried overnight in vacuo. Anal. Calcd for $C_{46}H_{38}P_2PtTl_2$: C, 43.96; H, 3.05. Found: C, 43.17; H, 3.10. ^{1}H NMR (DMSO-d_6): δ 5.43–6.23 (m, 8 H, Cp), 6.87–7.50 (m, 30 H, Ph). ^{31}P{^{1}H} NMR: δ(P) 10.4 ($^1J_{PtP}$ = 1840 Hz). ^{13}C{^{1}H} NMR: Cp at δ 106.00 (d, J_{PC} = 62 Hz), 109.80, 117.06; PPh at δ 126.51, 128.00 (d, J_{PC} = 63 Hz), 133.46, 138.80 (d, J_{PC} = 47 Hz); PtPh at δ 118.90, 125.54, 137.38, 164.49 (J_{PtC} not observed).

Preparation of [$PtPh_2$($Ph_2PC_5H_4$)$_2$ZrCl$_2$]. To a stirred solution of [$PtPh_2$(cod)] (0.115 g, 0.252 mmol) in CH_2Cl_2 (15 mL) was added ($Ph_2PC_5H_4$)$_2$ZrCl$_2$ (0.166 g, 0.251 mmol) in small portions over 0.5 h. The mixture was stirred overnight and then filtered, and the filtrate was evaporated to dryness. The resulting orange-red, oily material was washed with three 5-mL portions of petroleum ether to leave the product as an orange-red solid (0.226 g, 86%). ^{1}H NMR analysis revealed that the product contained 0.4 molecule of CH_2Cl_2/molecule of the complex; this could not be removed by prolonged pumping under high vacuum. Anal. Calcd for $C_{46.4}H_{38.8}Cl_{2.8}P_2PtZr$: C, 53.38; H, 3.75. Found: C, 52.70; H, 4.28.

Preparation of [PtClPh($Ph_2PC_5H_4$)$_2$ZrCl$_2$]. To a stirred solution of [PtClPh(cod)] (0.104 g, 0.250 mmol) in CH_2Cl_2 (15 mL) was added ($Ph_2PC_5H_4$)$_2$ZrCl$_2$ (0.166 g, 0.251 mmol) in small portions. The mixture was stirred overnight and then filtered, and the solvent was evaporated. The sticky, yellow residue was washed with toluene (3 mL) and petroleum ether (3 × 4 mL) and then dried in vacuo to give [PtClPh($Ph_2PC_5H_4$)$_2$ZrCl$_2$]·0.7 CH_2Cl_2 as a white solid (0.125 g, 49%). Anal. Calcd for $C_{40.7}H_{34.4}Cl_{4.4}P_2PtZr$: C, 47.56; H, 3.37. Found: C, 47.08; H, 3.74.

Preparation of *cis*-[$PtPh_2${PhP(C_5H_4)$_2$ZrCl$_2$}$_2$]. To a solution of PhP(C_5H_4)$_2$ZrCl$_2$ (0.199 g, 0.500 mmol) in tetrahydrofuran (10 mL) was added [$PtPh_2$(cod)] (0.115 g, 0.252 mmol) in small portions; then the mixture was stirred overnight. Following filtration, the solvent was evaporated and the residue was washed with petroleum ether (3 × 5 mL) to leave the product as a light yellow powder, which was dried in vacuo (0.230 g, 80%). Anal. Calcd for $C_{44}H_{36}Cl_4P_2PtZr_2$: C, 46.11; H, 3.17. Found: C, 45.92; H, 3.31.

Preparation of *trans*-[PtClPh{PhP(C_5H_4)$_2$ZrCl$_2$}$_2$]. This complex was prepared as above and was obtained as a light yellow powder in 83% yield. Anal. Calcd for $C_{38}H_{31}Cl_5P_2PtZr_2$: C, 41.33; H, 2.83. Found: C, 41.22; H, 3.92.

Reactions with ^{13}CO. In a typical experiment the Pt–Zr complex (ca. 20 mg) was suspended in $CDCl_3$ (0.5 mL) in a 5-mm NMR tube fitted with a stopcock. The solution was degassed by three freeze–pump–thaw cycles, then ^{13}CO was admitted to the tube, and the stopcock was closed. The mixture was allowed to stand at room temperature, and the progress of the reaction was monitored by ^{13}C and ^{31}P NMR spectroscopy.

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Registry No. (TlC_5H_4)$_2$PPh, 116232-60-1; Cl_2PPh, 644-97-3; TlC_5H_5, 34822-90-7; ($Ph_2PC_5H_4$)$_2$ZrCl$_2$, 100898-54-2; $ZrCl_4$(thF)$_2$, 21959-01-3; PhP(C_5H_4)$_2$ZrCl$_2$, 116232-52-1; *cis*-[$PtPh_2$($Ph_2PC_5H_4Tl$)$_2$], 116263-28-6; [$PtPh_2$(cod)], 12277-88-2; [$PtPh_2$($Ph_2PC_5H_4$)$_2$ZrCl$_2$], 116232-53-2; [PtClPh($Ph_2PC_5H_4$)$_2$ZrCl$_2$], 116232-54-3; *cis*-[$PtPh_2${PhP(C_5H_4)$_2$ZrCl$_2$}$_2$], 116232-55-4; *trans*-[PtClPh{PhP(C_5H_4)$_2$ZrCl$_2$}$_2$], 116232-56-5; [PtCl(COPh)($Ph_2PC_5H_4$)$_2$ZrCl$_2$], 116232-57-6; *trans,trans*-[PtCl(COPh){μ-($Ph_2PC_5H_4$)$_2$ZrCl$_2$}]$_2$, 116263-29-7; [PtClPh(dppp)], 96806-44-9; [PtCl(COPh)(dppp)], 96806-48-3; *cis*-[$PtPh_2$(CO){PhP(C_5H_4)$_2$ZrCl$_2$}], 116232-58-7; *trans*-[PtCl(COPh){PhP(C_5H_4)$_2$ZrCl$_2$}$_2$], 116232-59-8; [PtCl(COPh)(cod)], 76705-02-7; ($Ph_2PC_5H_4$)Tl, 85320-10-1.

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