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Arylgold(I) Complexes from Base-Assisted Transmetalation: Structures, NMR Properties, and Density-Functional Theory Calculations

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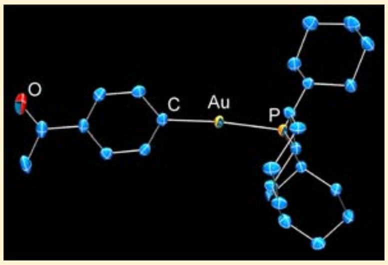
Supporting Information

ABSTRACT: The synthesis of gold(I) complexes of the type LAuR (L = PCy_3, IPr; R = aryl; IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) starting from LAuX (X = Br, OAc) and boronic acids in the presence of Cs_2CO_3 has been investigated. The reactions proceed smoothly in good to excellent yields over the course of 24−48 h in isopropyl alcohol at 50−55 °C. The aryl groups include a variety of functionalities and steric bulk, and in two cases, are heterocyclic. All of the products have been characterized by multinuclear NMR spectroscopy and elemental analysis and most by X-ray crystallography. This work affirms that, almost without exception, base-assisted auration is a useful and reliable way to form gold−carbon bonds.



INTRODUCTION

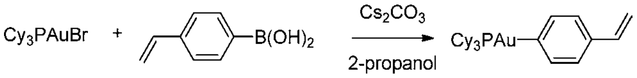
The organometallic chemistry of gold draws increasing attention. A growing body of work suggests that stable molecules and transient intermediates having gold−carbon bonds possess useful photophysical[1−15] and catalytic[16−23] properties. In continuing efforts to determine how attaching gold to aromatic hydrocarbons alters their photophysical properties,[24] we have demonstrated that *N*-heterocyclic carbene- and tricyclohexylphosphine-ligated pyrenylgold(I) complexes show phosphorescence that extends past 800 nm.[25] Naphthalene, when σ-bonded to (phosphine)gold(I) fragments, shows dual singlet- and triplet-state emission at room temperature. Emission is sensitive to the site of auration on the naphthalene core.[26] Numerous reports show that gold(I) efficiently catalyzes a variety of organic transformations and have implicated organogold(I) intermediates.[27−33] Huisgen [3 + 2] dipolar cycloaddition chemistry proceeds in high yield from the reaction of gold(I) azides with terminal alkynes to yield *C*-bound gold(I) triazolate complexes.[34,35] Recently, Hashmi and collaborators have reported [3 + 2] cycloaddition reactions of gold(I) isonitriles and azomethine ylides to yield abnormal *N*-heterocyclic carbene complexes of gold(I).[36] In the presence of copper(I), gold(I) alkynyls cycloadd to alkyl and benzyl azides with 1,4-regiochemistry.[37] Potential applications to human medicine have been demonstrated by the synthesis of (phosphine)gold(I) indolyl derivatives, where the indole nitrogen bears electron-withdrawing or -releasing groups. Two such compounds are promiscuous inhibitors of human kinase enzymes. They act synergistically with ^{137}Cs γ-radiation to elicit cell death in irradiated cultures.[38] Earlier syntheses of arylated gold(I) complexes have often relied on organolithium or Grignard reagents, which preclude sensitive functional groups.[39−43] There remains the possibility of transmetalation from organomercurials, with all their attendant hazards.[44]

Reports from this laboratory disclose that gold(I) displaces boron in reactions of (organophosphine)- or (*N*-heterocyclic carbene)gold(I) halides.[45−49] Sensitive functional groups are tolerated, and a range of phosphines and *N*-heterocyclic carbenes may be used as capping ligands on gold. In an effort to expand the scope of base-assisted transmetalation, we report the synthesis of new gold(I) organometallics relying on this protocol. Several are crystallographically characterized. Complications from rearrangement of an allenylboronate and protodeboronation of an unprotected indole are discussed alongside density-functional theory computations. We find that base-assisted transmetalation, although robust, can be complicated for Brønsted acidic or rearrangeable substrates.

RESULTS AND DISCUSSION

Synthesis. Gold(I) bromides were treated with a variety of boronic acids as shown in Scheme 1. Compound **6** is representative. A base appears to be necessary in these reactions, although we have not tested this for every substrate. The reaction solvent (2-propanol) dissolved both base and boronic acid at 50 °C. Products precipitate readily; most have

Scheme 1



6
91%

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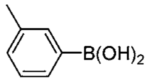
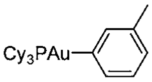
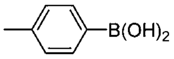
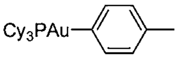
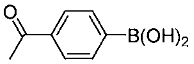
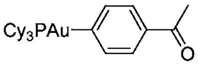
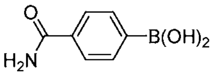
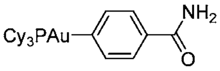
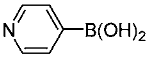
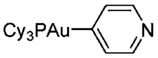
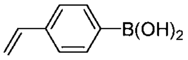
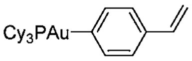
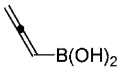
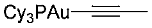
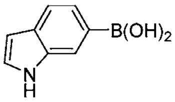
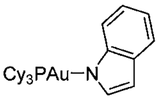
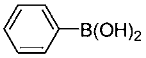
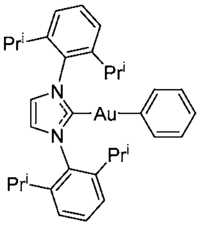
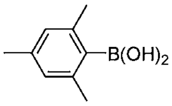
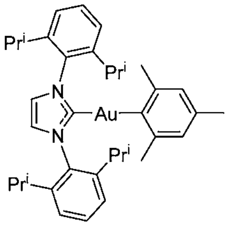
Table 1. Gold(I) Products, Yields, and Designation of Compounds

Gold(I) precursor	Arylboronic acid	No. equiv. boronic acid	Reaction time (h)	Product	Isolated yield
Cy_3PAuBr		1.8	24	 **1**	57%
Cy_3PAuBr		1.9	24	 **2**	73%
Cy_3PAuBr		2.0	36	 **3**	85%
Cy_3PAuBr		2.0	36	 **4**	19%
Cy_3PAuBr		2.0	24	 **5**	88%
Cy_3PAuBr		1.7	24	 **6**	91%
Cy_3PAuBr		2.0	24	 **7**	74%
$Cy_3PAuOAc$ **8**		2.0	24	 **9**	39%
IPrAuBr		2.0	24	 **10**	88%
IPrAuBr		3.7	48	 **11**	87%

little or no solubility in 2-propanol. In all cases, the workup followed a simple protocol that was performed in air. The solvent was removed by rotary evaporation, followed by extraction into toluene or benzene, filtration through Celite and collection of the filtrate, removal of solvent, and trituration (or crystallization) with pentane. In some cases, trace boronic acid remained, so an additional wash with ice-cold methanol was necessary.

Potentially sensitive functional groups on the boronic acids (or boropinacolate ester) include amide, ketone, aldehyde, allenyl, and amine. However, in our hands, isolated yields are high. Results appear in Table 1.

Most reactions were executed using a gold(I) bromide as starting material, but in one case (Entry 8), the product was formed in higher yield when a gold(I) acetate was used as the starting reagent (39% isolated yield). An analogous reaction with Cy_3PAuBr as starting material gave the same product in 9% yield. The choice of gold(I) bromides as reactants was circumstantial; the corresponding gold(I) chlorides often transmetallate with comparable efficiency.[47,49] Product **11** indicates that steric bulk does not inhibit transmetalation, as found earlier.[50] Table 1 shows that most reactions proceed in moderate to excellent yield, except **4** and **9**.

Crystallography. Eight compounds were characterized by single crystal X-ray diffraction. While most reactions yielded the expected products, the combination of crystallographic and NMR analysis proves that, as solids and in solution, two (**7** and **9**) did not. Typical phosphine-ligated arylgold(I) complexes are the isomeric tolyls **1** and **2**, Figures S1 and S2, Supporting Information. Isomers **1** and **2** differ in solubility. Whereas the *para*-isomer **2** is insoluble in hexanes and pentane and crystallized readily, the *meta*-isomer **1** has some solubility in pentane and does not easily crystallize. The density as calculated from the unit cell contents suggests that the more symmetric isomer **2** packs more efficiently than **1** (1.645 vs 1.628 kg m^{-3}, respectively). Both compounds crystallize in the same space group. Thus, packing may account for some of the difference in solubility. Bond angles and lengths at gold are

Table 2. Crystallographic Data for 1–3, 5, 7–9, and 11 at 100 K[a]

	1	2	3	5	7	8	9	11
formula	$C_{25}H_{40}AuP$	$C_{25}H_{40}AuP$	$C_{26}H_{40}AuOP$	$C_{23}H_{37}AuNP$	$C_{21}H_{36}AuP$	$C_{20}H_{36}AuO_2P \cdot 1/2\ C_6H_6$	$C_{26}H_{39}AuNP$	$C_{36}H_{47}AuN_2$
fw	568.51	568.51	596.52	555.47	516.43	575.48	593.52	704.72
crystal system	triclinic	triclinic	monoclinic	triclinic	monoclinic	triclinic	orthorhombic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1P2_1P2_1$	$C2/c$
a, Å	9.170(2)	8.9329(5)	11.3384(8)	9.4903(7)	17.478(3)	9.074(2)	8.2372(7)	20.220(2)
b, Å	10.837(3)	10.5661(6)	16.1535(1)	11.3240(9)	7.5496(1)	10.612(2)	17.1313(2)	16.0965(2)
c, Å	12.505(3)	12.5173(7)	13.7362(1)	11.6943(9)	17.326(3)	12.973(3)	17.2431(2)	23.180(4)
α, deg	80.933(4)	96.753(1)		76.596(1)		107.093(4)		
β, deg	71.423(4)	101.367(1)	104.374(1)	67.719(1)	118.546(2)	100.704(4)		114.506(2)
γ, deg	82.979(4)	92.489(1)		81.084(1)		96.207(4)		
V, Å^3	1159.9(5)	1147.5(1)	2437.1(3)	1128.1(2)	2008.3(6)	1155.5(4)	2433.2(4)	6864.7(2)
Z	2	2	4	2	4	2	4	8
D_{calcd}, mg m^{-3}	1.628	1.645	1.626	1.635	1.708	1.654	1.620	1.364
T, K	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
μ, mm^{-1}	6.418	6.487	6.117	6.598	7.404	6.450	6.124	4.310
θ_{min}, θ_{max}, deg	2.46, 30.39	1.67, 28.28	2.24, 30.53	2.40, 30.53	2.65, 31.53	3.04, 30.48	2.36, 31.89	1.68, 28.28
GOF[b] on F^2	1.058	1.056	1.052	1.087	1.191	1.128	1.020	1.006
final R indices[c] $[I > 2\sigma(I)]$ R_1	0.0169	0.0215	0.0297	0.0205	0.0402	0.0424	0.0200	0.0241
wR_2	0.0418	0.0534	0.0797	0.0532	0.1342	0.1179	0.0426	0.0491

[a] Mo Kα radiation, $\lambda = 0.71073$ Å. [b] $\mathrm{GOF} = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$; n = number of reflections, p = number of parameters refined. [c] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

unremarkable. Table 2 summarizes crystallographic data for the new structures.

Figures S3 and S4, Supporting Information, show thermal ellipsoid representations of **3** and **5**, respectively. Metrics at gold are typical. The lack of disorder at the acetyl functionality of **3** is surprising considering that there should be a negligible energy difference between this conformer and the 180° rotated (about the C4–C7 bond) conformer. Examination of the packing diagram does not suggest any kind of intermolecular interactions that might lead to exclusivity of conformation. In the case of **5**, the pyridyl nitrogen atom is not hydrogen bonded nor does it form any close contact with the gold atom of an adjacent molecule.

Compound **7** is a rearranged product. Its structure appears as Figure 1. Whereas the starting reagent is an allenylboronic acid, **7** is a gold(I) propynyl. The propynyl ligand is nearly linear (∠C19–C20–C21 = 178.6(9)°), whereas the angle at the metalated carbon atom deviates slightly from linearity (∠Au1–C19–C20 = 173.4(8)°). This angle is marginally more acute than observed for other crystallographically characterized phosphine-ligated alkynylgold(I) complexes.[51−55] Metrics involving gold are normal.

Density-functional theory (DFT) calculations were performed on allenyl and alkynyl model complexes having trimethylphosphine ligands instead of tricyclohexylphosphine. This substitution is made for computational tractability. Geometries were optimized without imposed symmetry or other restraints. Harmonic frequency calculations confirm that the converged structures are potential energy minima. Full computational details appear in the Experimental Section. We find that the propynyl complex is more stable than the allenyl isomer. This conclusion is based on sums of electronic and thermal free energies at 298 K. The gold(I) alkynyl is calculated to be 5.34 kcal mol^{-1} stabler than the allenyl, eq 1. If the allenyl does form, its isomerization to the alkynyl is predicted to be spontaneous.

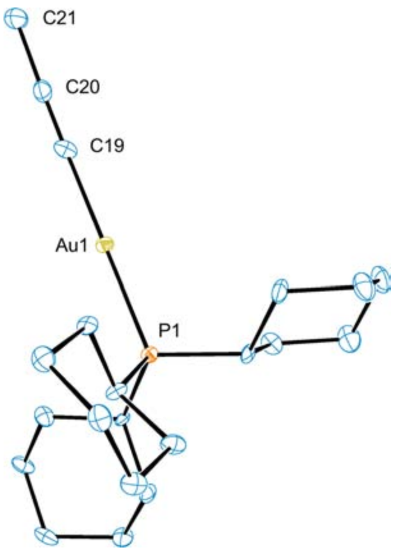
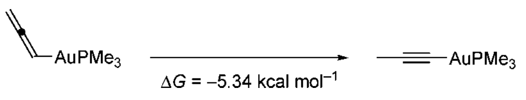


Figure 1. Thermal ellipsoid representation of **7** showing 50% probability ellipsoids and partial atom-labeling. Hydrogen atoms are omitted for clarity; unlabeled atoms are carbon. Selected bond lengths (Å) and angles (°): Au1–C19 2.007(8), Au1–P1 2.286(2), C19–C20 1.195(1), C20–C21 1.474(1), Au1–C19–C20 173.4(8), C19–C20–C21 178.6(9), and C19–Au1–P1 175.5(2).



(1)

Figure 2 depicts the crystal structures of **8** and **9**. The synthesis of **9** (from **8**) proceeded in lower yield than those of the other gold(I) species here. Both the ^{31}P and ^{1}H NMR spectra suggested the product was not carbon-bound. This hypothesis was supported by X-ray crystallography (Figure 2b), which shows that the product contains a nitrogen-bound indolyl ligand that has undergone protodeboronation.[44]

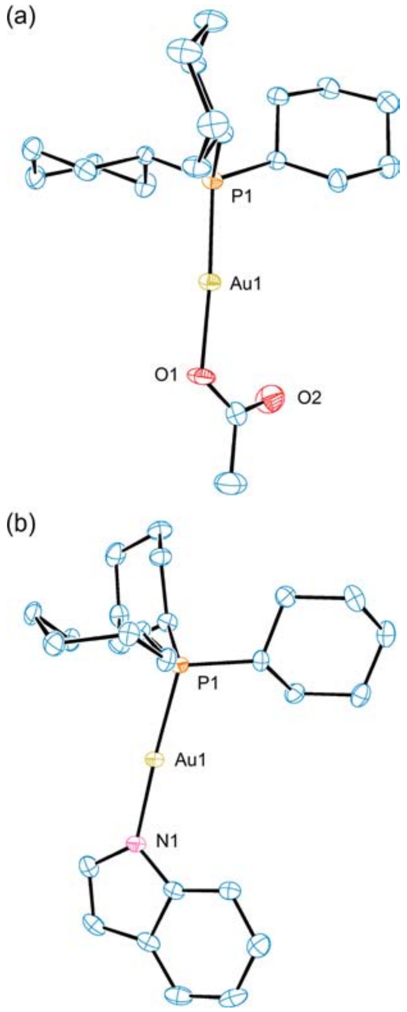
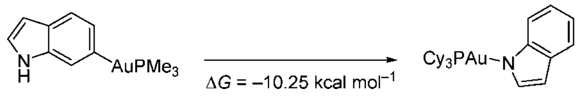


Figure 2. Thermal ellipsoid depictions of (a) **8** and (b) the coupling product **9** showing 50% probability ellipsoids and partial atom-labeling. Hydrogen atoms are omitted for clarity; unlabeled atoms are carbon. Selected bond lengths (Å) and angles (°): (**8**) Au1−O1 2.052(4), Au1−P1 2.2245(2), and O1−Au1−P1 173.88(1). (**9**) Au1−N1 2.028(3), Au1−P1 2.2465(9), and N1−Au1−P1 177.16(8).

DFT calculations were conducted on model (indolyl)gold(I) complexes, again with PMe_3 in place of PCy_3. The free-energy gain on isomerizing from *C*-bound to *N*-bound product is substantial, eq 2. This result, alongside the isolation of **9**, is



(2)

notable in that indole is a privileged structure in biology.[56] Recent work[38] shows that gold(I) complexes of *N-protected* indoles are broadly cytotoxic to malignant cell lines. At least some such compounds potentiate the cell-killing action of ionizing radiation. For bioactive indoles where gold binds to *carbon*, protection of the indole nitrogen appears prudent.

An advantage of acetate complex **8** as a carrier of gold is its solubility in alcohols. Its structure, Figure 2a, is similar to that of other gold(I) acetates.[57,58] As is common for d^{10} group 11 centers, acetate binds in a κ^1-fashion,[59] and the metal adopts a linear geometry. Comparison of the phosphorus−gold bond lengths shows that acetate is a weaker *trans*-influencer than any *C*-bonded aryl considered here. The same observation holds for the *N*-indolyl ligand of **9**. As the structure of **9** shows, the indolyl ligand has undergone protodeboronation with loss of the $B(OH)_2$ group, and NMR suggests this protodeboronation reaction has no indolyl byproducts after workup.

(*N*-Heterocyclic carbene)gold(I) precursors also undergo base-assisted transmetalation.[25] Accordingly, a typical (NHC)-gold(I) bromide was reacted with two arylboronic acids. Although spectroscopic and microanalytical data support the formation of the phenyl complex **10**, repeated attempts at crystallographic characterization proved unsuccessful. However, in the case of the bulkier analogue **11**, a suitable crystal was found. The structure of **11** appears as Figure 3. The potency of the *trans* influence of the mesityl ligand is clear when compared to (IPr)AuBr (Au−C = 1.975(5) Å).[60] Steric clash between the mesityl and IPr ligands is minimized in three ways. First, ∠C1−Au1−C28 is nearer 180° than in any other complex in this investigation. Second, the torsion angle between the mean mesityl plane (C_6 ring) and the mean imidazolium plane (67.5°) is such that the mesityl ligand resides in the cleft formed by the 2,6-diisopropylphenyl substituents. Third, one 2,6-diisopropylphenyl group rotates such that one of its isopropyl groups cants away from the proximal methyl group (of the mesityl ligand). Overall, these features confer C_1 symmetry on **11**.

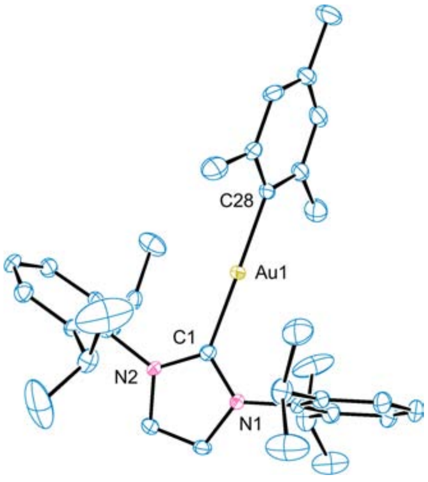


Figure 3. Thermal ellipsoid representation of **11** showing 50% probability ellipsoids and partial atom-labeling. Hydrogen atoms are omitted for clarity, and unlabeled atoms are carbon. Selected bond lengths (Å) and angles (°): Au1−C1 2.026(3), Au1−C28 2.038(2), C1−Au1−C28 178.0(1), N2−C1−N1 104.1(2), N2−C1−Au1 128.34(2), and N1−C1−Au1 127.53(2).

NMR Spectroscopy. The most diagnostic spectroscopic signatures are the ^{31}P or ^{13}C (carbene) resonances of each product. All spectra were measured in C_6D_6. In general, ^{31}P signals for arylgold(I) complexes appeared between 57 and 58 ppm, with electron-withdrawing substituted aryl ligands leading to slightly lower-field signals. This observation corresponds with earlier work.[45] The ^{31}P signal of other products (**7**−**9**) had lower-field resonances than the arylgold(I) complexes, and this was particularly useful in the determination of **9** as an *N*-bound product. Furthermore, there is a rough correlation between Au−P bond length and ^{31}P chemical shift. (Tricyclohexylphosphine)gold(I) complexes show Au−P bond lengths that fall in a narrow range, 2.224(2) Å (**8**) to 2.3058(6) Å (**2**). Corresponding ^{31}P chemical shifts (in C_6D_6)

fall in an approximately 2 ppm window (centered at ~57.5 ppm). The observed chemical shift of **9** (50.1 ppm) immediately suggested that **9** was not *C*-bound, and X-ray crystallography confirms this conclusion for solid **9**. The bond length-chemical shift correlation has been observed before with ^{13}C nuclei (a gold(I)-carbene series)[58] and other metals with various nuclei.[61−64] If the correlation in ref 58 holds, then the gold(I)-carbene carbon bond distance in **11** is longer than in **10**. That is, mesityl exerts a stronger *trans* influence than phenyl, as ^{13}C carbene-carbon chemical shifts are 200.88 and 198.39 ppm, respectively. This supposition is intuitively appealing. Provided steric effects do not materially alter binding; a mesityl ligand should have more electron density at the bound carbon because of its three methyl substituents.

^{1}H NMR was also useful for determining solution conformation and corroborating identities of certain products (**4**, **7**, and **9**) in particular. All products except **1** have spectroscopic signatures that indicate local mirror symmetry of the aryl ligand. For **4**, mass spectrometry and ^{1}H NMR suggested that the desired *para*-aurated benzamide was the isolated product. For **7**, the lack of multiple allenyl resonances suggested that the allenyl group was no longer present. In fact, the observed doublet was that of a propynyl methyl group that was coupled to phosphorus. Under the experimental conditions, the allenyl group had rearranged. Lowering the temperature (room temperature with longer stirring) led to the same result. As discussed above, **9** was found to be *N*-bound by X-ray crystallography, and this was corroborated by ^{1}H and ^{31}P NMR. Furthermore, the observation of six signals by ^{1}H NMR suggested protodeboronation, as proved to be the case. Although we have not observed this in gold transmetalation chemistry up to this point, this phenomenon has been observed in the literature.[65−67] Protodeboronation reactions have been shown to be catalyzed separately by the presence of base[68] and metal ions;[69] therefore, it is not surprising the conditions here (involving *both* a base and a metal ion) lead to clean protodeboronation. Note that this selectivity for nitrogen is opposite that observed in the reaction of $(PPh_3)AuN_3$ with terminal alkynes, in which the [3 + 2] cycloaddition product is exclusively *C*-bound.[34,35]

■ CONCLUSIONS

The base-mediated transmetalation of aryl groups from boron to gold has been elaborated. The reaction generally proceeds in high yield and circumvents functional group incompatibilities of organolithium and Grignard chemistry. Bulky phosphines and *N*-heterocyclic carbenes are suitable ancillary ligands on gold(I), and acetate has been found to be a suitable leaving group on gold(I), conferring solubility in alcohol onto the gold substrate. As anticipated, a phosphine-ligated, pyridine-containing product shows no evidence for any equilibrium between the *N*-bound and *P*-bound isomers. Furthermore, in the case of **11** (an IPr-ligated mesitylgold(I) complex), considerable steric hindrance does not prevent formation of the organogold complex in high yield. The transmetalation reactions generally proceeded as expected, but in two cases, an unexpected rearrangement and isomerization product were cleanly formed. DFT investigations corroborate the spontaneity of these rearrangements; future investigations may address if these rearrangements can be exploited to yield new organometallic products.

■ EXPERIMENTAL SECTION

All solvents and reagents were used as received. Microanalyses (C, H, and N) were performed by Quantitative Technologies Inc. NMR spectra (^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$) were recorded on a Varian AS-400 spectrometer operating at 399.7, 100.5, and 161.8 MHz, respectively.

Cy_3PAu(3-tolyl) (1). In 5 mL of 2-propanol were suspended Cs_2CO_3 (101 mg, 0.31 mmol) and 3-tolylboronic acid (41 mg, 0.30 mmol). Cy_3PAuBr (93 mg, 0.17 mmol) was added to the reaction mixture, and the mixture was stirred for 24 h at 50 °C, cooled, and taken to dryness in vacuo. The dry solid was extracted with ~15 mL of benzene, filtered, and washed thoroughly with ethylene glycol (2 × 5 mL) and water (5 mL) in a separatory funnel. The benzene layer was collected and dried with $MgSO_4$, filtered, and taken to a residue in vacuo. The residue was triturated with pentane to liberate a white free-flowing solid. Yield: 54 mg (57%). ^{1}H NMR (C_6D_6): δ 7.91−7.97 (m, 2H, $C_6H_4(CH_3)$), 7.47 (td, 1H, $C_6H_4(CH_3)$, J = 1.6, 7.2 Hz), 7.08 (d, 1H, $C_6H_4(CH_3)$, J = 7.2 Hz), 2.35 (s, 3H, $C_6H_4(CH_3)$), 0.92−1.90 (m, 33H, C_6H_{11}) ppm. $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 57.5 (s) ppm. Anal. Calcd. for $C_{25}H_{40}AuP$: C, 52.82; H, 7.09. Found: C, 52.66; H, 7.27.

Cy_3PAu(4-tolyl) (2). In 5 mL of 2-propanol were suspended Cs_2CO_3 (94 mg, 0.29 mmol) and 4-tolylboronic acid (39 mg, 0.29 mmol). Cy_3PAuBr (84 mg, 0.15 mmol) was added, and this mixture was heated at ~50 °C for 24 h. After cooling, the suspension was taken to dryness in vacuo, extracted into benzene, filtered through Celite, and taken to dryness in vacuo. The residue was washed with pentane, dried, re-extracted into a minimum of benzene, and filtered, and pentane vapor was diffused to cause separation of colorless crystals. The crystals were washed with a small amount of cold methanol and pentane and dried. Yield: 63 mg (73%). ^{1}H NMR (C_6D_6): δ 8.05 (dd, 2H, $C_6H_4(CH_3)$, J = 4.8, 8.0 Hz), 7.35 (d, 2H, $C_6H_4(CH_3)$, J = 8.0 Hz), 2.31 (s, 3H, $C_6H_4(CH_3)$), 0.91−1.88 (m, 33H, C_6H_{11}) ppm. $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 57.6 (s) ppm. Anal. Calcd. for $C_{25}H_{40}AuP$: C, 52.82; H, 7.09. Found: C, 53.01; H, 7.16.

Cy_3PAu(4-acetylphenyl) (3). In 5 mL of 2-propanol were suspended Cs_2CO_3 (104 mg, 0.32 mmol) and 4-acetylphenylboronic acid (53 mg, 0.32 mmol). To this suspension was added Cy_3PAuBr (89 mg, 0.16 mmol), and the mixture was stirred at 50 °C for 30 h. After cooling, the mixture was stripped of solvent in vacuo, extracted into benzene, filtered through Celite, and taken to dryness in vacuo. The white solid was washed thoroughly with pentane, dried, extracted into benzene, filtered through Celite, and concentrated to saturation. Pentane vapor was diffused to cause separation of colorless crystals, which were washed with cold methanol and pentane, dried, and collected. Yield: 81 mg (85%). ^{1}H NMR (C_6D_6): δ 8.06−8.16 (m, 4H, $C_6H_4(COCH_3)$), 2.21 (s, 3H, $C_6H_4(COCH_3)$), 0.92−1.86 (m, 33H, C_6H_{11}). $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 57.3 (s) ppm. Anal. Calcd. for $C_{26}H_{40}AuOP$: C, 52.35; H, 6.76. Found: C, 52.57; H, 6.80.

Cy_3PAu(4-benzamide) (4). In 5 mL of 2-propanol were suspended Cs_2CO_3 (97 mg, 0.30 mmol) and 4-carbamoylphenylboronic acid (51 mg, 0.31 mmol). To this suspension was added Cy_3PAuBr (83 mg, 0.15 mmol), and the mixture was stirred at 50 °C for 30 h. After cooling, the mixture was stripped of solvent in vacuo, extracted into benzene, filtered through Celite, and taken to dryness in vacuo. The white solid was washed thoroughly with pentane, dried, extracted into benzene, filtered through Celite, and concentrated to saturation. Pentane vapor was diffused to cause separation of colorless crystals. Yield: 17 mg (19%). ^{1}H NMR (C_6D_6): δ 8.02−8.06 (m, 2H, $C_6H_4(CONH_2)$), 7.90 (dd, 2H, $C_6H_4(CONH_2)$, J = 1.6, 8.0 Hz), 0.90−1.89 (m, 33H, C_6H_{11}). $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 57.3 (s) ppm. MS (ESI^{+}): m/z = 620.2326 $(M + Na)^{+}$. Anal. Calcd. for $C_{25}H_{39}AuNOP$: C, 50.25; H, 6.58; N, 2.34. Found: C, 50.36; H, 6.68; N, 2.31.

Cy_3PAu(4-pyridyl) (5). In 5 mL of 2-propanol were suspended Cs_2CO_3 (95 mg, 0.29 mmol) and 4-pyridylboronic acid (36 mg, 0.29 mmol). To this suspension was added Cy_3PAuBr (81 mg, 0.15 mmol), and the mixture was stirred at 50 °C for 24 h. After cooling, the mixture was stripped of solvent in vacuo, extracted into benzene, filtered through Celite, and taken to dryness by rotary evaporation.

The solid was triturated with pentane, and the pentane was decanted. The solid was extracted into benzene, filtered through Celite, and concentrated past the point of saturation. Pentane vapor was diffused to complete separation of light brown crystals, which were washed with cold methanol and pentane, dried, and collected. Yield: 70 mg (88%). ^{1}H NMR (C_6D_6): δ 8.81−8.84 (m, 2H, C_6H_4N), 7.72−7.76 (m, 2H, C_6H_4N), 0.90−1.93 (m, 33H, C_6H_{11}). ^{31}P{^{1}H} NMR (C_6D_6): δ 57.2 (s) ppm. Anal. Calcd. for $C_{23}H_{37}AuNP$: C, 49.73; H, 6.71; N, 2.52. Found: C, 50.02; H, 6.75; N, 2.47.

Cy$_3$PAu(4-styryl) (6). A flask was loaded with Cs_2CO_3 (34 mg, 0.10 mmol), 4-styrylboronic acid (16 mg, 0.11 mmol), and Cy$_3$PAuBr (36 mg, 0.065 mmol); 2-propanol (3 mL) was added. The mixture was stirred at 50 °C for 24 h. After cooling, the mixture was stripped of solvent in vacuo, extracted into toluene, filtered through Celite, and taken to dryness by rotary evaporation. The solid was triturated with pentane, and the pentane was decanted. The solid was washed with cold methanol, dried, and collected. Yield: 34 mg (91%). ^{1}H NMR (C_6D_6): δ 8.06−8.11 (m, 2H, $C_6H_4(C_2H_3)$), 7.58 (d, 2H, $C_6H_4(C_2H_3)$, J = 7.2 Hz), 6.79 (dd, 1H, $C_6H_4(C_2H_3)$, J = 10.4, 17.6 Hz), 5.73 (dd, 1H, $C_6H_4(C_2H_3)$, J = 1.2, 17.6 Hz), 5.07 (dd, 1H, $C_6H_4(C_2H_3)$, J = 1.2, 10.4 Hz) 0.86−1.85 (m, 33H, C_6H_{11}). ^{31}P{^{1}H} NMR (C_6D_6): δ 57.3 (s) ppm. Anal. Calcd. for $C_{26}H_{40}AuP$: C, 53.79; H, 6.94. Found: C, 53.87; H, 6.95.

Cy$_3$PAu(propynyl) (7). A flask was loaded with Cs_2CO_3 (46 mg, 0.14 mmol) and Cy$_3$PAuBr (43.5 mg, 0.078 mmol). To this flask was added allenylboropinacolate ester (26 mg, 0.16 mmol) in 3 mL of degassed 2-propanol. The mixture was stirred at 50−55 °C for 36 h. After cooling, the mixture was stripped of solvent in vacuo, extracted into toluene, filtered through Celite, and taken to dryness by rotary evaporation. The solid was triturated with pentane, and the pentane was decanted. The solid was collected and dried; it was analytically pure. Yield: 30 mg (74%). ^{1}H NMR (C_6D_6): δ 2.05 (d, 3H, CC−CH_3, J = 1.6 Hz), 0.81−1.75 (m, 33H, C_6H_{11}). ^{31}P{^{1}H} NMR (C_6D_6): δ 56.7 (s) ppm. Anal. Calcd. for $C_{21}H_{36}AuP$: C, 48.84; H, 7.03. Found: C, 48.83; H, 7.10.

Cy$_3$PAu(OAc) (8). In 5 mL of benzene was dissolved Cy$_3$PAuCl (81 mg, 0.16 mmol), and to this solution was added 1.08 equiv (28 mg, 0.17 mmol) of Ag(OAc). The resultant suspension was stirred for 2 h and filtered through Celite. The solution was concentrated to a residue via rotary evaporation. The residue was triturated with pentane until it became a free-flowing, colorless solid. The solid was collected and dried. Yield: 76 mg (90%). ^{1}H NMR (C_6D_6): δ 2.32 (s, 3H, CO_2CH_3), 0.84−1.68 (m, 33H, C_6H_{11}) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ 47.9 (s) ppm. This compound was used without further purification.

Cy$_3$PAu(*N*-indolyl) (9). *Method A.* In 3 mL of 2-propanol were suspended Cs_2CO_3 (61 mg, 0.19 mmol), 5-indoleboronic acid (30 mg, 0.19 mmol), and Cy$_3$PAuBr (52 mg, 0.093 mmol), and the mixture was stirred at 50 °C for 24 h. After cooling, the mixture was stripped of solvent in vacuo, extracted into toluene, filtered through Celite, and taken to dryness by rotary evaporation. The residue was triturated with pentane, and the pentane was decanted. The solid was extracted into toluene and filtered through Celite, and pentane vapor was diffused to complete separation of colorless crystals (sometimes coated with a minute amount of purple material). The crystals were collected and dried. Yield: 5 mg (9%). ^{1}H NMR (C_6D_6): δ 8.25 (d, 1H, J = 8.0 Hz), 8.13 (d, 1H, J = 8.0 Hz), 7.78 (d, 1H, J = 2.4 Hz), 7.48 (t, 1H, J = 7.6 Hz), 7.36 (t, 1H, J = 7.6 Hz), 7.05 (m, 1H), 0.88−1.70 (m, 33H, C_6H_{11}). ^{31}P{^{1}H} NMR (C_6D_6): δ 50.1 ppm. Anal. Calcd. for $C_{26}H_{39}AuNP$: C, 52.61; H, 6.62; N, 2.36. Found: C, 52.69; H, 6.70; N, 2.24.

Method B. In 3 mL of 2-propanol were suspended Cs_2CO_3 (80 mg, 0.25 mmol), 5-indoleboronic acid (40 mg, 0.25 mmol), and Cy$_3$PAu(OAc) (66 mg, 0.12 mmol), and the mixture was stirred at 50 °C for 24 h. After cooling, the mixture was stripped of solvent in vacuo, extracted into toluene, filtered through Celite, and taken to dryness by rotary evaporation. The solid was triturated with pentane, and the pentane was decanted. The solid was extracted into toluene and filtered through Celite, and pentane vapor was diffused to complete separation of colorless crystals (coated with a minute amount of purple material). The crystals were collected and dried. Yield: 29 mg (39%). This product was spectroscopically identical to **9**.

IPrAu(phenyl) (10). A flask was loaded with IPrAuBr[60] (81 mg, 0.12 mmol), phenylboronic acid (31 mg, 0.25 mmol), and Cs_2CO_3 (83 mg, 0.26 mmol). To this flask was added 2-propanol (5 mL), and the suspension was stirred at ∼55 °C for 24 h. After cooling, the suspension was rotovapped to dryness, extracted into benzene, filtered, and taken to dryness. It was extracted again into benzene, filtered, and evaporated to saturation, and finally, pentane vapor was diffused into the saturated solution. The crystalline solid that separated was collected and dried. Yield: 71 mg (88%). ^{1}H NMR (C_6D_6): δ 7.52 (dd, 2H, C_6H_5, J = 1.6, 8.0 Hz), 7.18−7.24 (m, 4H, IPr (*para*-H) + C_6H_5), 7.07 (d, 4H, IPr (*meta*-H), J = 8.0 Hz), 6.99 (tt, 1H, *para*-C_6H_5, J = 1.6, 8.0 Hz), 6.30 (s, 2H, imidazole C*H*), 2.66 (sep, 4H, C*H*($CH_3)_2$, J = 6.8 Hz), 1.48 (d, 12H, CH($CH_3)_2$, J = 6.8 Hz), 1.09 (d, 12H, CH($CH_3)_2$, J = 7.2 Hz). ^{13}C{^{1}H} NMR (C_6D_6): δ 198.39 (s, *C* carbene), 169.89 (s, CH aromatic), 145.89 (s, CH aromatic), 141.19 (s, CH aromatic), 134.99 (s, CH aromatic), 130.48 (s, CH aromatic), 127.08 (s, CH aromatic), 124.69 (s, CH aromatic), 124.12 (s, CH aromatic), 122.45 (s, CH imidazole), 29.00 (s, CH($CH_3)_2$), 24.77 (s, CH($CH_3)_2$), 23.86 (s, CH($CH_3)_2$) ppm. Anal. Calcd. for $C_{33}H_{41}AuN_2$: C, 59.81; H, 6.24; N, 4.23. Found: C, 59.96; H, 6.19; N, 4.16.

IPrAu(mesityl) (11). A flask was loaded with IPrAuBr (63 mg, 0.095 mmol), mesitylboronic acid (57 mg, 0.35 mmol), and Cs_2CO_3 (108 mg, 0.35 mmol). To this flask was added 2-propanol (4 mL), and the suspension was stirred at ∼55 °C for 48 h. After cooling, the suspension was evaporated to dryness, extracted into toluene, filtered, and taken to dryness. The solid was triturated with pentane and collected, washed with cold methanol, and dried. Yield: 58 mg (87%). ^{1}H NMR (C_6D_6): δ 7.26 (t, 2H, *para*-C_6H_3, J = 8.0 Hz), 7.10 (d, 4H, *meta*-C_6H_3, J = 8.0 Hz), 6.97 (s, 2H, mesityl C*H*), 6.34 (s, 2H, imidazole C*H*), 2.65 (sep, 4H, C*H*($CH_3)_2$, J = 6.8 Hz), 2.27 (s, 3H, *para*-mesityl singlet), 2.23 (s, 6H, *ortho*-mesityl singlet), 1.43 (d, 12H, CH($CH_3)_2$, J = 6.8 Hz), 1.09 (d, 12H, CH($CH_3)_2$, J = 6.8 Hz) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 200.88 (s, *C* carbene), 167.11 (s, *ipso* mesityl *C*), 146.59 (s, CH aromatic), 146.07 (s, CH aromatic), 135.25 (s, CH aromatic), 133.02 (s, CH aromatic), 130.33 (s, CH aromatic), 126.02 (s, CH aromatic), 124.03 (s, CH aromatic), 122.26 (s, CH imidazole), 29.02 (s, CH($CH_3)_2$), 26.33 (s, *ortho*-mesityl CH_3), 24.63 (s, CH($CH_3)_2$), 23.99 (s, CH($CH_3)_2$), 21.41 (s, *para*-mesityl CH_3) ppm. Anal. Calcd. for $C_{36}H_{47}AuN_2$: C, 61.18; H, 6.99; N, 3.96. Found: C, 61.08; H, 6.85; N, 3.90.

X-ray Structure Determination. Compounds **1**−**3**, **5**, and **8** were crystallized by diffusion of pentane into saturated benzene solutions. Compounds **7**, **9**, and **11** were crystallized by diffusion of pentane into saturated toluene solutions. Single crystal X-ray data were collected on a Bruker AXS SMART APEX CCD diffractometer using monochromatic Mo Kα radiation with omega scan technique. The unit cells were determined using SMART and SAINT+. All structures were solved by direct methods and refined by full matrix least-squares against F^2 with all reflections using SHELXTL. Refinement of extinction coefficients was found to be insignificant. All nonhydrogen atoms were refined anisotropically. All other hydrogen atoms were placed in standard calculated positions, and all hydrogen atoms were refined with an isotropic displacement parameter 1.5 (CH_3) or 1.2 (all others) times that of the adjacent carbon or nitrogen atom.

Calculations. Density-functional theory calculations were performed within the Gaussian 09 program suite.[70] All calculations were spin-restricted and employ the parameter-free PBE0 functional.[71] Calculations, including geometry optimizations, include continuum solvation in benzene using the integral equation formalism of the polarizable continuum model of Tomasi and co-workers.[72,73] The Stuttgart-Dresden basis set and pseudopotential were used for gold;[74] the TZVP basis set of Godbelt, Andzelm, and co-workers was applied for nonmetal atoms.[75] Geometry optimizations proceeded in redundant internal coordinates without imposed symmetry or any other constraints. Harmonic frequency calculations on optimized structures returned all real vibrational frequencies. Sums of electronic and thermal free energies were calculated from harmonic vibrational frequencies without scaling.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data in .cif format and optimized Cartesian coordinates of model complexes. 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 interests.

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■ REFERENCES

(1) Forward, J. M.; Fackler, J. P., Jr.; Assefa, Z. Photophysical and Photochemical Properties of Gold(I) Complexes. In *Optoelectronic Properties of Inorganic Compounds*; Roundhill, D. M., Fackler, J. P., Jr., Eds.; Plenum Press: New York, 1999; pp 195−226.

(2) He, X. M.; Yam, V. W.-W. *Coord. Chem. Rev.* **2011**, *255*, 2111.

(3) Yam, V. W.-W.; Cheng, E. C. C. *Chem. Soc. Rev.* **2008**, *37*, 1806.

(4) Vogt, R. A.; Peay, M. A.; Gray, T. G.; Crespo-Hernández, C. E. *J. Phys. Chem. Lett.* **2010**, *1*, 1205.

(5) Lu, W.; Kwok, W.-M.; Ma, C.; Chan, C. T.-L.; Zhu, M.-X.; Che, C.-M. *J. Am. Chem. Soc.* **2011**, *133*, 14120.

(6) Chao, H.-Y.; Lu, W.; Li, Y. Q.; Chan, M. C. W.; Che, C.-M.; Cheung, K.-K.; Zhu, N. Y. *J. Am. Chem. Soc.* **2002**, *124*, 14696.

(7) Che, C.-M.; Chao, H.-Y.; Miskowski, V. M.; Li, Y. Q.; Cheung, K.-K. *J. Am. Chem. Soc.* **2001**, *123*, 4985.

(8) Lu, W.; Xiang, H.-F.; Zhu, N. Y.; Che, C.-M. *Organometallics* **2002**, *21*, 2343.

(9) Fernández, E. J.; Laguna, A.; López-de-Luzuriaga, J. M.; Monge, M.; Montiel, M.; Olmos, M. E. *Inorg. Chem.* **2007**, *46*, 2953.

(10) de la Riva, H.; Nieuwhuyzen, M.; Fierro, C. M.; Raithby, P. R.; Male, L.; Lagunas, M. C. *Inorg. Chem.* **2006**, *45*, 1418.

(11) Elbjeirami, O.; Yockel, S.; Campana, C. F.; Wilson, A. K.; Omary, M. A. *Organometallics* **2007**, *26*, 2550.

(12) Elbjeirami, O.; Omary, M. A.; Stender, M.; Balch, A. L. *Dalton Trans.* **2004**, 3173.

(13) Vickery, J. C.; Olmstead, M. M.; Fung, E. Y.; Balch, A. L. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1179.

(14) Elbjeirami, O.; Gonser, M. W. A.; Stewart, B. N.; Bruce, A. E.; Bruce, M. R. M.; Cundari, T. R.; Omary, M. A. *Dalton Trans.* **2009**, 1522.

(15) Heckler, J. E.; Zeller, M.; Hunter, A. D.; Gray, T. G. *Angew. Chem., Int. Ed.* **2012**, *51*, 5924.

(16) Rudolph, M.; Hashmi, A. S. K. *Chem. Soc. Rev.* **2012**, *41*, 2448.

(17) Wang, W.; Hammond, G. B.; Xu, B. *J. Am. Chem. Soc.* **2012**, *134*, 5697.

(18) Zhang, Z.; Liu, C.; Kinder, R. E.; Han, X.; Qian, H.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2006**, *128*, 9066.

(19) Han, X.; Widenhoefer, R. A. *Angew. Chem., Int. Ed.* **2006**, *45*, 1747.

(20) Luzung, M. R.; Markham, J. P.; Toste, F. D. *J. Am. Chem. Soc.* **2004**, *126*, 10858.

(21) Hashmi, A. S. K.; Braun, I.; Nösel, P.; Schädlich, J.; Wieteck, M.; Rudolph, M.; Rominger, F. *Angew. Chem., Int. Ed.* **2012**, *51*, 4456.

(22) Hashmi, A. S. K.; Ramamurthi, T. D.; Rominger, F. *Adv. Synth. Catal.* **2010**, *352*, 971.

(23) Hashmi, A. S. K.; Braun, I.; Rudolph, M.; Rominger, F. *Organometallics* **2012**, *31*, 644.

(24) Gray, T. G. *Comments Inorg. Chem.* **2007**, *28*, 181.

(25) Partyka, D. V.; Esswein, A. J.; Zeller, M.; Hunter, A. D.; Gray, T. G. *Organometallics* **2007**, *26*, 3279.

(26) Gao, L.; Peay, M. A.; Partyka, D. V.; Updegraff, J. B., III; Teets, T. S.; Esswein, A. J.; Zeller, M.; Hunter, A. D.; Gray, T. G. *Organometallics* **2009**, *28*, 5669.

(27) Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2010**, *49*, 5232.

(28) Nieto-Oberhuber, C.; López, S.; Echavarren, A. M. *J. Am. Chem. Soc.* **2005**, *127*, 6178.

(29) Johansson, M. J.; Gorin, D. J.; Staben, S. T.; Toste, F. D. *J. Am. Chem. Soc.* **2005**, *127*, 18002.

(30) Nieto-Oberhuber, C.; Muñoz, M. P.; López, S.; Jiménez-Núñez, E.; Nevado, C.; Herrero-Gómez, E.; Raducan, M.; Echavarren, A. M. *Chem.—Eur. J.* **2006**, *12*, 1677.

(31) Morita, N.; Krause, N. *Angew. Chem., Int. Ed.* **2006**, *45*, 1897.

(32) Ye, L.; Wang, Y.; Aue, D. H.; Zhang, L. *J. Am. Chem. Soc.* **2012**, *134*, 31.

(33) Tsui, E. Y.; Müller, P.; Sadighi, J. P. *Angew. Chem., Int. Ed.* **2008**, *47*, 8937.

(34) Partyka, D. V.; Updegraff, J. B., III; Zeller, M.; Hunter, A. D.; Gray, T. G. *Organometallics* **2007**, *26*, 183.

(35) Robilotto, T. J.; Alt, D. S.; von Recum, H. A.; Gray, T. G. *Dalton Trans.* **2011**, *40*, 8083.

(36) Hashmi, A. S. K.; Riedel, D.; Rudolph, M.; Rominger, F.; Oeser, T. *Chem.—Eur. J.* **2012**, *18*, 3827.

(37) Partyka, D. V.; Gao, L.; Teets, T. S.; Updegraff, J. B., III; Deligonul, N.; Gray, T. G. *Organometallics* **2009**, *28*, 6171.

(38) Craig, S.; Gao, L.; Lee, I.; Gray, T. G.; Berdis, A. J. *J. Med. Chem.* **2012**, *55*, 2437.

(39) Schmidbaur, H.; Schier, A. In *Comprehensive Organometallic Chemistry III*; Crabtree, R.; Mingos, M., Eds.; Elsevier: Cambridge, U. K., 2006; Vol. 2, Section 2.05.

(40) Porter, K. A.; Schier, A.; Schmidbaur, H. *Pespectives in Organometallic Chemistry*; Royal Society of Chemistry: 2003; Vol. 287, p 74.

(41) Fernández, E. J.; Laguna, A.; Olmos, M. E. *Adv. Organomet. Chem.* **2005**, *52*, 77.

(42) Schmidbaur, H.; Grohmann, A.; Olmos, M. E. In *Gold: Progress in Chemistry, Biochemistry and Technology*; Schmidbaur, H., Ed.; Wiley: Chichester, 1999.

(43) Schmidbaur, H. In Organogold Compounds. In *Gmelin Handbuch der Anorganischen Chemie*, 8th ed.; Slawisch, A., Ed.; Springer-Verlag: Berlin, 1980.

(44) Partyka, D. V. *Chem. Rev.* **2011**, *111*, 1529.

(45) Partyka, D. V.; Zeller, M.; Hunter, A. D.; Gray, T. G. *Angew. Chem.* **2006**, *45*, 8188.

(46) Peay, M. A.; Heckler, J. E.; Deligonul, N.; Gray, T. G. *Organometallics* **2011**, *30*, 5071.

(47) Partyka, D. V.; Teets, T. S.; Zeller, M.; Updegraff, J. B., III; Hunter, A. D.; Gray, T. G. *Chem.—Eur. J.* **2012**, *18*, 2100.

(48) Gao, L.; Niedzwiecki, D. S.; Deligonul, N.; Zeller, M.; Hunter, A. D.; Gray, T. G. *Chem.—Eur. J.* **2012**, *18*, 6316.

(49) Hashmi, A. S. K.; Ramamurthy, T. D.; Rominger, F. *J. Organomet. Chem.* **2010**, *694*, 592.

(50) Partyka, D. V.; Updegraff, J. B., III; Zeller, M.; Hunter, A. D.; Gray, T. G. *Organometallics* **2009**, *28*, 1666.

(51) Gao, L.; Partyka, D. V.; Updegraff, J. B., III; Deligonul, N.; Gray, T. G. *Eur. J. Inorg. Chem.* **2009**, 2711.

(52) Vicente, J.; Chicote, M.-T.; Abrisqueta, M.-D.; Jones, P. G. *Organometallics* **1997**, *16*, 5628.

(53) Bruce, M. I.; Hall, B. C.; Skelton, B. W.; Smith, M. E.; White, A. H. *J. Chem. Soc., Dalton Trans.* **2002**, 995.

(54) Schuster, O.; Liau, R.-Y.; Schier, A.; Schmidbaur, H. *Inorg. Chim. Acta* **2005**, *358*, 1429.

(55) Liau, R.-Y.; Schier, A.; Schmidbaur, H. *Organometallics* **2003**, *22*, 3199.

(56) de Sa Alves, F. R.; Barreio, E. J.; Fraga, C. A. M. *Mini Rev. Med. Chem.* **2009**, *9*, 782.
(57) Schneider, S. K.; Hermann, W. A.; Herdtweck, E. *Z. Anorg. Allg. Chem.* **2003**, *629*, 2363.
(58) Baker, M. V.; Barnard, P. J.; Brayshaw, S. K.; Hickey, J. L.; Skelton, B. W. *J. Chem. Soc., Dalton Trans.* **2005**, 37.
(59) Mankad, N.; Gray, T. G.; Laitar, D. S.; Sadighi, J. P. *Organometallics* **2004**, *23*, 1191.
(60) de Frémont, P.; Singh, R.; Stevens, E. D.; Petersen, J. L.; Nolan, S. P. *Organometallics* **2007**, *27*, 1376.
(61) Mobley, T. A.; Gandour, R.; Gillis, E. P.; Nti-Addae, K.; Palchaudhuri, R.; Rajbhandari, P.; Tomson, N.; Vargas, A.; Zheng, Q. *Organometallics* **2005**, *24*, 3897.
(62) Craw, J. S.; Bacskay, G. B.; Hush, N. S. *J. Am. Chem. Soc.* **1994**, *116*, 5937.
(63) Albinati, A.; Naegali, R.; Starzewski, K. H. A.; Ostoja, P.; Pregosin, P. S.; Ruegger, H. *Inorg. Chim. Acta* **1983**, *76*, L231.
(64) Mather, G. G.; Pidcock, A.; Rapsey, G. J. N. *J. Chem. Soc., Dalton Trans.* **1973**, 2095.
(65) Klingensmith, L. M.; Bio, M. M.; Moniz, G. A. *Tetrahedron Lett.* **2007**, *48*, 8242.
(66) Kuivila, H. G.; Nahebedian, K. V. *J. Am. Chem. Soc.* **1961**, *83*, 2164.
(67) Nahebedian, K. V.; Kuivila, H. G. *J. Am. Chem. Soc.* **1961**, *83*, 2167.
(68) Kuivila, H. G.; Reuwer, J. F.; Mangravite, J. A. *Can. J. Chem.* **1963**, *41*, 3081.
(69) Kuivila, H. G.; Reuwer, J. F.; Mangravite, J. A. *J. Am. Chem. Soc.* **1964**, *86*, 2666.
(70) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision A.02*; Gaussian, Inc.: Wallingford CT, 2009.
(71) Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, *110*, 6158.
(72) Barone, V.; Cossi, M.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3210.
(73) Cancès, E.; Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3032.
(74) Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1987**, *86*, 866.
(75) Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Can. J. Chem.* **1992**, *70*, 560−571.