ORGANOMETALLICS

Syntheses, X-ray Crystal Structures, and Solution Behavior of Cationic, Two-Coordinate Gold(I) η^2 -Diene Complexes

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Supporting Information

ABSTRACT: A family of cationic gold π -diene complexes of the form $\{[P(t-Bu)_2 o-biphenyl]Au(\eta^2-diene)\}^+SbF_6^-$ were isolated in >80% yield from reaction of various dienes with a mixture of $[P(t-Bu)_2 o$ -biphenyl]AuCl and AgSbF₆ and were characterized by spectroscopy and, in four cases, by X-ray crystallography. Solution and solid-state analysis of these com-



plexes established selective binding of gold to the less substituted C=C bond of the diene in the case of dienes that possessed differentially substituted C=C bonds. ¹³C NMR analysis and evaluation of the relative binding affinities of substituted dienes point to a bonding model in which the gold-alkene interaction is stabilized via donation of electron density from the uncomplexed C=C bond to the complexed C=C bond of the diene. Variable-temperature NMR analysis of gold π -diene complexes revealed fluxional behavior consistent with facile ($\Delta G^{\ddagger} = 9.6 - 11.9 \text{ kcal mol}^{-1}$) intramolecular exchange of the complexed and uncomplexed C=C bonds of the diene ligand.

INTRODUCTION

In recent years, considerable effort has been directed toward the development of cationic gold(I) complexes as catalysts for the π -activation of C-C multiple bonds toward addition of carbon and heteroatom nucleophiles.¹ Included in this family of transformations is the gold(I)-catalyzed intermolecular 1,2-addition of the X–H bond of a sulfonamide,² carbamate,³ thiol,⁴ or indole⁵ to the less substituted C=C bond of a conjugated diene and also the gold(I)-catalyzed intramolecular 1,4-addition of the N-H bond of a sulfonamide to a conjugated diene.⁶ The selective 1,2-addition of the nucleophile across the less substituted C=C bond in the gold(I)-catalyzed intermolecular hydrofunctionalization of conjugated dienes distinguishes these transformations from other transition metal-catalyzed diene hydrofunctionalization processes, which typically occur with net 1,4-addition^{7,8} and/or telomerization.^{8,5}

Gold(I)-catalyzed diene hydrofunctionalization has been proposed to occur via initial π -coordination of the diene to gold, either through the less substituted C=C bond³⁻⁶ or to both C=C bonds,² followed by outer-sphere addition of the nucleophile and subsequent protodeauration. An outer-sphere pathway involving attack of the nucleophile on a gold η^2 -diene intermediate was further supported by computational analysis of the gold(I)-catalyzed intramolecular hydroamination of 3-methyl-1,3-pentadiene with benzyl carbamate.¹⁰ Despite the potential role of cationic gold(I) π -diene complexes in the gold(I)catalyzed hydrofunctionalization of conjugated dienes, no wellcharacterized gold π -diene complexes have been documented. ¹¹ As such, information regarding the structure, bonding, and fluxional behavior of cationic gold(I) π -diene complexes is limited to that provided by computational analysis⁷ or that gleaned from related gold π -alkene,¹²⁻¹⁴ alkyne,¹⁴⁻¹⁶ arene,^{16,17} and allene

complexes.^{18,19} Here we report the synthesis, solution and solidstate structure, and fluxional behavior of cationic, two-coordinate gold(I) η^2 -diene compounds that contain a di-*tert*-butyl *o*-biphenylphosphine ligand.

RESULTS AND DISCUSSION

Synthesis of Gold η^2 -Diene Complexes. Cationic, twocoordinate gold(I) η^2 -diene complexes were synthesized employing a procedure similar to that used to prepare cationic gold(I) η^2 -alkene complexes.¹² For example, treatment of a methylene chloride suspension of $[P(t-Bu)_2 o$ -biphenyl]AuCl and $AgSbF_6$ (1:1) with *trans*-1,3-pentadiene (10 equiv) for 6 h at room temperature followed by filtration and removal of volatile materials led to the isolation of $\{ [P(t-Bu)_2 o-biphenyl] \}$ Au[η^2 -(E)-H₂C=C(H)C(H)=C(H)Me]}⁺SbF₆⁻ (1) in 93% yield as an air and thermally stable white solid (Scheme 1). Likewise, the cationic gold(I) η^2 -diene complexes {[P(t-Bu)₂obiphenyl]Au(η^2 -diene)}+SbF_6^- [diene = 4-methyl-1,3-pentadiene (2), 2,4-dimethyl-1,3-pentadiene (3), 1,3-butadiene (4), 2,3-dimethyl-2-butene (5), 1,3-cyclohexadiene (6), and 1,4-cyclohexadiene (7) were isolated in >80% yield as air- and thermally stable white solids. Although stable indefinitely in the solid state, these gold π -diene complexes were only modestly stable in solution and tended to decompose when concentrated. This behavior complicated purification, and solutions of these complexes typically contained traces (\sim 5%) of the free diene. More specifically, complexes 2 and 3 were effectively crystallized from concentrated CH₂Cl₂ solutions, which, in the case of 2, also

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produced X-ray quality crystals. Conversely, crystallization of 1, 4, and 7 from concentrated CH₂Cl₂ solutions produced X-ray quality crystals but also formed amorphous material that degraded the bulk purity of the sample. Attempted crystallization of 5 and 6 led to degradation of the sample without crystal formation. Nevertheless, complexes 1–7 displayed satisfactory combustion analysis, were unambiguously characterized in solution by ¹H, ¹³C, and ³¹P NMR spectroscopy, and, in cases of complexes 1, 2, 4, and 7, were characterized by X-ray crystallography.

X-ray Crystal Structure of 1. Slow diffusion of hexanes into a CH₂Cl₂ solution of 1 at 4 °C gave colorless crystals of 1 suitable for single-crystal X-ray analysis (Figure 1). The crystal structure of 1 established a monomeric complex with the trans-1, 3-pentadiene ligand η^2 -bonded to gold through the less substituted C1=C2 bond. Complex 1 adopts a distorted linear conformation with a P-Au-alkene(cent) angle of 169.3° and with the diene ligand unsymmetrically bonded to gold with a shorter Au–C1 and longer Au–C2 interaction ($\Delta d = 0.113$ Å). The coordinated C1=C2 bond of the diene is elongated relative to the uncomplexed C3=C4 bond ($\Delta d = 0.049$ Å), and the diene moiety adopts a near planar s-trans configuration with a C1-C2-C3-C4 dihedral angle of 169.9°. The diene ligand is positioned such that the angle defined by Au-C1-C2 is rotated by $\sim 12^{\circ}$ relative to the plane defined by Au-P-C14 with the C=C(H)Me group directed away from the protruding phenyl ring and along the Au-P-C14 plane. The protruding phenyl group of the o-biphenyl phosphine moiety is not perpendicular to the P-bound aryl ring, but instead is rotated toward the C6 quaternary carbon atom with a C14-C19-C20-C21 dihedral angle of 70.6°. The distance between the gold atom and the plane of the protruding phenyl group is 2.88 Å with a gold to C_{ipso} distance of Au - C20 = 3.018 Å, suggesting the presence of a weak Ar-arene interaction. Similar Au-arene interactions have been observed for gold dialkyl(o-biphenyl)phosphine^{17,20,21} and related gold complexes,²² although the Au-arene distance of 1 is shorter than is typically observed (Au-arene_(plane) = 3.0-3.2 Å,^{17,20} $Au - C_{ipso} = 3.16 - 3.36 \text{ Å}).^2$

The η^2 -coordination of the *trans*-1,3-pentadiene ligand in complex 1, as opposed to η^4 -coordiation, is not surprising owing to the pronounced tendency of gold(I) to form two-coordinate 14-electron complexes, rather than three-coordinate, 16-electron complexes.²³ Nevertheless, η^2 -complexes of conjugated dienes are rare, as most transition metal diene complexes display a



Figure 1. ORTEP drawing of 1. Ellipsoids are shown at the 50% probability level. Counterion and hydrogen atoms are omitted for clarity. Selected bond distances (Å), bond angles (deg), and torsional angles (deg): Au-C1 = 2.226(7), Au-C2 = 2.332(5), C1-C2 = 1.363(9), C2-C3 = 1.394(7), C3-C4 = 1.313(10), C4-C5 = 1.492(12), Au-arene_(plane) = 2.88, Au-C20 = 3.018, P-Au-C1=C2_(cent) = 163.3, C1-C2-C3 = 128.4(5), C2-C3-C4 = 126.8(5), C1-C2-C3-C4 = 169.9(8), C14-C19-C20-C21 = 70.6(9), C14-C19-C20-C25 = 120.0(8).

strong preference toward η^4 -coordination of the diene.²⁴ Examples of transition metal η^2 -diene complexes include three-coordinate palladium, platinum, and nickel complexes that contain both an η^2 -1,3-butadiene ligand and a chelating bis(phosphine) ligand.²⁵ Thermolysis of $(\eta^5$ -C₅Me₅)W(σ -alkyl)(π -allyl) complexes generates 16-electron η^2 -diene intermediates that can be trapped as their 18-electron PMe₃ adducts.²⁶ Photolysis of tungsten,^{27,28} molybdenum,^{28,29} rhenium,³⁰ and cobalt³¹ carbonyl compounds in the presence of diene also forms η^2 -diene compounds. Similarly, treatment of molybdenum η^4 -diene compounds with a tertiary phosphine or CO forms the corresponding molybdenum η^2 -diene compound.³² Iron η^2 -diene complexes have been isolated from rearrangements of iron-allylidene compounds with triphenylcarbenium-hexafluorophosphate.³⁴

Solution-State Structure and Fluxional Behavior of 1. The solution-state structure and fluxional behavior of trans-1,3-pentadiene complex 1 was probed spectroscopically. In the ¹³C NMR spectrum of 1 at $-80 \,^{\circ}C_{2}^{35}$ the resonance corresponding to the C1 carbon atom of bound *trans*-1,3-pentadiene (δ 90.6, d, $J_{\rm CP}$ = 10.1 Hz) was shifted ~24 ppm to lower frequency relative to that of the free diene (δ 114.4), while the C2 (δ 137.1) and C3 (δ 129) diene resonances of 1 were only slightly perturbed ($\Delta\delta$ <4 ppm) relative to the resonances of free *trans*-1,3-pentadiene (Table 1). In comparison, the C4 diene resonance of 1 (δ 144.3) was shifted to higher frequency by \sim 14 ppm relative to that of free diene (δ 129.8). The ¹H NMR spectrum of 1 mirrored that of the ¹³C NMR spectrum. For example, the C1 diene protons of 1 [δ 4.17, 4.11] were shifted ~0.8 ppm to lower frequency relative to those of free *trans*-1,3-pentadiene (δ 5.06, 4.93), while the C2 (δ 6.51) and C3 (δ 5.99) diene resonances of 1 differed by ≤ 0.2 ppm relative to those of free *trans*-1, 3-pentadiene. In comparison, the C4 proton of 1 (δ 6.26) was shifted to higher frequency by \sim 0.5 ppm relative to that of free diene.

| | | | C1 | C2 | | C3 | | C4 | | | |
|---------|-----------|----------------|-------------------|-----------------------------|----------------|-------------------|-----------------------------|--------------------|-----------------------------|----------------|-----------------------------|
| complex | temp (°C) | δ (ppm) | $J_{\rm PC}$ (Hz) | $\Delta\delta~({ m ppm})^a$ | δ (ppm) | $J_{\rm PC}$ (Hz) | $\Delta\delta~({ m ppm})^a$ | δ (ppm) | $\Delta\delta~({ m ppm})^a$ | δ (ppm) | $\Delta\delta~({ m ppm})^a$ |
| 1 | -80 | 90.6 | 10.0 | -23.8 | 137.1 | | -0.1 | 129^{b} | -3.6 | 144.3 | 14.5 |
| 2 | 25 | 90.6 | 15.0 | -23.8 | 134.3 | | 0.8 | 123.5 | -2.6 | 153.1 | 17.5 |
| 3 | 25 | 91.7 | 16.3 | -21.9 | 158.7 | | 16.3 | 125.1 ^c | -2.3 | 149.4 | 15.5 |
| 4^d | -90 | 94.9 | 12.6 | -22.6 | 133.5 | 2.5 | -4.6 | 133.3 | -4.8 | 128.6 | 11.1 |
| 5^d | -60 | 91.9 | 15.0 | -21.2 | 154.7 | | 10.9 | 140.2 | -3.4 | 124.2 | 11.1 |
| 6^d | -70 | 114.7 | 8.3 | -11.6 | 117.4 | 6.2 | -7.0 | 121.1 | -3.3 | 136.4 | 10.1 |

Table 1. ¹³C NMR Chemical Shifts and J_{PC} of the Diene sp² Carbon Atoms of Complexes 1–6 in CD₂Cl₂ and Chemical Shift Difference ($\Delta \delta$) Relative to Free Diene

^{*a*} Negative $\Delta\delta$ corresponds to a shift of the complex to lower frequency relative to free diene; positive $\Delta\delta$ corresponds to a shift of the complex to higher frequency relative to free diene. ^{*b*} C3 diene resonance overlapped with an aromatic *o*-biphenyl resonance. ^{*c*} J_{PC} = 5.2 Hz. ^{*d*} C1 and C2 are defined as the gold-bound C=C bond.

The spectroscopy of the cationic gold 1-hexene complex $\{ [P(t-Bu)_{2}o-biphenyl] Au[\eta^2-H_2C=C(H)(CH_2)_3CH_3] \}^+ SbF_6^-$ (8) serves as a point of comparison for the spectroscopy of diene complex 1.¹² The ¹³C NMR spectrum of 8 displays a large shift $(\Delta \delta \approx -16)$ of the C1 alkene carbon atom to lower frequency and small shift of the C2 carbon atom to higher frequency ($\Delta \delta \approx \sim 2$) relative to the corresponding resonances of free 1-hexene. Likewise, the terminal alkene protons of 8 are shifted \sim 0.5 ppm to lower frequency, while the internal alkenes protons are shifted \sim 0.3 ppm to higher frequency. We have attributed this behavior to unsymmetric binding of the alkene to gold with stronger interaction between Au-C1 relative to Au-C2, a contention that was supported by X-ray crystallographic studies.¹² Therefore, the significant shifts of the C1 diene carbon atom and C1 diene protons of 1 to higher frequency indicate that the diene binds to gold through the C1=C2 bond, as was observed in the solid state. The most notable features of the NMR spectroscopy of 1 were the pronounced shifts of the C4 carbon resonance and C4 vinyl protons to higher frequency relative to free diene. These observations point to stabilization of the gold $-\pi$ interaction of 1 through donation of electron density from the uncomplexed C3=C4 bond to the complexed C1=C2 bond, leading to depletion of electron density at the C4 diene carbon atom of 1.

Because the C1=C2 bond of *trans*-1,3-pentadiene is prochiral, a static structure for 1 possesses diastereotopic *tert*-butyl groups. Indeed, at -80 °C the ¹³C NMR spectrum of 1 displayed a pair of phosphorus-coupled doublets at δ 37.0 and 36.9 (J_{CP} = 24 Hz), corresponding to the quaternary tert-butyl carbon atoms (Figure 2). As the temperature was raised, these doublets both shifted to higher frequency and broadened, forming a single phosphorus-coupled doublet at δ 38.2 (J_{CP} = 24 Hz) at -50 °C that sharpened further upon warming to room temperature. The temperature-dependent behavior of the quaternary tertbutyl ¹³C resonances of 1 was independent of free trans-1,3pentadiene (150 mM), which argues against an intermolecular pathway for interconversion of the phosphorus-bound tert-butyl groups. We were unable to satisfactorily simulate the temperature-dependent ¹³C NMR spectra of 1, perhaps due in part to the temperature-dependent chemical shifts of the quaternary tert-butyl carbon atoms.

The presence of equivalent *tert*-butyl groups in the ¹³C NMR spectrum of 1 at ≤ -50 °C points to a facile fluxional process that exchanges the prochiral faces of the *trans*-1,3-pentadiene ligand. Although exchange of alkene π -faces without displacement has been documented in the case of a cationic rhenium complex,³⁶



Figure 2. Temperature dependence of the quaternary *tert*-butyl 13 C NMR resonance of 1 from -50 to -80 °C in CD₂Cl₂.

a more likely mechanism for racemization of 1 involves intramolecular exchange of the complexed and uncomplexed C=C bonds of the *trans*-1,3-pentadienyl ligand of 1 through *s*-*cis* and *strans* η^4 -diene transition states and intermediates (Scheme 2). For example, intramolecular ligand exchange of (*R*)-1 via the *s*-*cis* η^4 -diene intermediate *s*-*cis*-I would form the undetected C3=C4-bound isomer 1a (Scheme 2). A second intramolecular ligand exchange via the *s*-*trans* η^4 -diene intermediate *s*-*trans*-I would form (*S*)-1. Note that both *s*-*cis* and *s*-*trans* η^4 -diene intermediates are required for racemization of 1; a mechanism involving either *s*-*cis* or *s*-*trans* η^4 -diene intermediates would lead to exchange of the complexed and uncomplexed diene C=C bonds of 1 without racemization (see below).

X-ray Crystal Structures of 2, 4, and 7. In addition to *trans*-1,3-pentadiene complex 1, 4-methyl-1,3-butadiene complex 2, 1,3-butadiene complex 4, and 1,4-cyclohexadiene complex 7 were analyzed by X-ray crystallography (Figures 3–5). Refinement of 2 was complicated by an orientational disorder of the 4-methyl-1,3-pentadiene ligand, which precluded meaningful analysis of the bond distances and angles within the 4-methyl-1,3-pentadiene ligand. Nevertheless, the crystal structure of 2 revealed a distorted linear η^2 -diene complex with the gold atom bound unsymmetrically to the less substituted C1=C2 bond of the diene with a shorter Au-C1 and longer Au-C2 interaction, as was observed for complex 1 (Figure 3). In the major conformer of 2 (2a, 57% occupancy), the diene ligand is positioned so that the Au-C1-C2 plane is rotated by 77.4° relative to the Au-P-C15 plane with the C3 carbon atom directed away from

the protruding phenyl ring of the *o*-biphenylphosphine ligand. In the minor conformer (**2b**, 43% occupancy), the coordinated C1=C2 bond is bound through the opposite π -face relative to **2a** and is positioned such that the Au-C1-C2 plane rotated by 66.8° relative to the Au-P-C15 plane with the C3 carbon atom directed toward the protruding phenyl group. In both **2a** and **2b**, the protruding phenyl group of the *o*-biphenyl phosphine moiety is rotated toward the C7 quaternary carbon atom with C15-C20-C21-C22 = 80.2° and with an Au-arene_(plane) distance of 3.02 Å.

Similar to 2, complex 4 suffered from an orientational disorder of the 1,3-butadiene ligand. In both conformers of 4, gold adopts a distorted linear conformation $[P-Au-alkene_{(cent)} = 166-168^{\circ}]$ with the η^2 -butadiene ligand bound unsymmetrically to gold through a shorter Au-C1 and longer Au-C2 interaction $(\Delta d = 0.9-0.10 \text{ Å};$ Figure 4). In the major conformer of 4 (4a, 64% occupancy), the coordinated C1=C2 bond of the diene (as defined by the Au-C1-C2 plane) is rotated \sim 38° relative to the Au-P-C14 plane with the unbound C3=C4 group directed away from the *o*-phenyl ring and along the Au-P-C14 plane. In the minor conformer of 4 (4b, 36% occupancy), the diene ligand is bound through the opposite π -face relative to 4a and is positioned such that the Au-C1-C2 plane is rotated \sim 20° relative





to the Au–P–C14 plane with the unbound C3=C4 moiety directed away from the proximal phenyl group. In both conformers, the protruding phenyl group of the *o*-biphenyl phosphine moiety is rotated toward the C9 quaternary carbon atom with a C13–C14–C19–C24 dihedral angle of 63.5° and with an Au–arene_(plane) distance of 2.96 Å.

Complex 7, which contains a nonconjugated 1,4-cyclohexadiene ligand, adopts a slightly distorted linear conformation $(P-Au-alkene_{(cent)})$ angle of 171.3°) with the diene ligand bound more symmetrically to gold (Δd Au-C1/Au-C2 = 0.031 Å; Figure 5) than was observed for acyclic 1,3-diene complexes 1, 2, and 4. The coordinated C1=C2 bond of the cyclohexadiene ligand is positioned roughly parallel to the protruding phenyl ring of the *o*-biphenyl moiety with the remainder of the cyclohexadiene ligand directed away from the proximal phenyl group. The two aryl rings of the *o*-biphenylphosphine ligand are perpendicular to one another with a C15-C20-C21-C22 dihedral angle of 91.0°. Within the 1,4-cyclohexadiene moiety, the coordinated C1=C2 bond is elongated by 0.038 Å relative to the uncomplexed C3=C4 bond, and the C-C=C-C groupings associated with both the complexed and uncomplexed C=C bonds are planar, with C6-C1-C2-C3 and C3-C4-C5-C6 dihedral angles of <2°. Interestingly, the 1,4-cyclohexadiene ligand adopts a boat-like conformation with an angle of $\sim 18^{\circ}$ between the C6–C1–C2–C3 and C3-C4-C5-C6 planes with the concave face directed toward the *tert*-butyl groups.

Spectroscopy of Complexes 2–6. The vinylic protons and sp² diene carbon atoms of complexes **3**, **4**, and **6** were unambiguously assigned from the ¹H and ¹³C NMR spectra supported by various combinations of ¹H–¹H COSY, HMQC, HMBC, and variable-temperature ¹³C NMR spectroscopy. The vinylic protons and sp² diene carbon atoms of complexes **2** and **5** were confidently assigned from the ¹H and ¹³C NMR spectra and by analogy to the spectroscopy of complexes **1**, **3**, **4**, and **6**. As was the case with **1**, assignment of ¹³C resonances was aided by the presence of phosphorus coupling to the C1 diene carbon atom with *J*_{CP} ranging from 12.6 to 16.3 Hz for acyclic diene complexes **2**–**5** and 8.3 Hz for cyclohexadiene complex **6** (Table 1). Details regarding these ¹H and ¹³C assignments are provided in the Supporting Information.

Several points regarding the ¹³C NMR spectroscopy of complexes 1-6 are worth noting (Table 1). Each of the complexes



Figure 3. ORTEP drawings of 2a (left structure) and 2b (right structure). Ellipsoids are shown at the 50% probability level. Counterion and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) for 2a: Au-C1 = 2.245(4), Au-C2 = 2.292(8), $Au-arene_{(plane)} = 3.02$, Au-C21 = 3.036, $P-Au-C1=C2_{(cent)} = 169.06$, C15-C20-C21-C22 = 80.2(6), C15-C20-C21-C26 = 108.8(6). Selected, unique bond distances (Å) and angles (deg) for 2b: Au-C1 = 2.245(4), $Au-C1=C2_{(cent)} = 162.49$.



Figure 4. ORTEP drawings of 4a (left structure) and 4b (right structure). Ellipsoids are shown at the 50% probability level. Counterion and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) for 4a: Au-C1 = 2.215(4), Au-C2 = 2.312(3), C1-C2 = 1.376(5), C2-C3 = 1.456(5), C3-C4 = 1.326(7), $Au-arene_{(plane)} = 2.92$, Au-C19 = 3.064, $P-Au-C1=C2_{(cent)} = 165.98$, C1-C2-C3 = 123.2(5), C2-C3-C4 = 121.9(6), C1-C2-C3-C4 = 167.2(4), C13-C14-C19-C20 = 125.76(17), C13-C14-C19-C24 = 63.5(2). Selected, unique bond distances (Å) and angles (deg) for 4b: Au-C1 = 2.212(7), Au-C2 = 2.300(6), C1-C2 = 1.351(11), C2-C3 = 1.474(11), C3-C4 = 1.346(14), $P-Au-C1=C2_{(cent)} = 167.82$, C1-C2-C3 = 123.3(10), C2-C3-C4 = 120.2(11), C1-C2-C3-C4 = 172.1(8).



Figure 5. ORTEP drawing of 7 with ellipsoids shown at the 50% probability level. Counterion and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Au-C1 = 2.264(5), Au-C2 = 2.295(5), C1-C2 = 1.352(7), C2-C3 = 1.496(8), C3-C4 = 1.509(9), C4-C5 = 1.314(8), C5-C6 = 1.504(8), $Au-arene_{(plane)} = 3.01$, Au-C21 = 3.060, $P-Au-C1=C2_{(cent)} = 171.69$, C1-C2-C3 = 121.4(5), C2-C3-C4 = 112.7(5), C3-C4-C5 = 123.2(5), C4-C5-C6 = 123.3(5), C2-C1-C6 = 123.7(5), C14-C19-C20-C21 = 15.7(7), C15-C20-C21-C22 = 91.0.

2–6 displayed a shift of the C1 diene carbon resonance to lower frequendy and a shift of the uncomplexed C4 diene carbon to higher frequency relative to the corresponding resonances of free diene, as was observed for 1 (Table 1). In the cases of complexes 2 and 3, which possess dissimilarly substituted C=C double bonds, these features established binding of the diene to gold in solution through the less substituted C1=C2 bond, as was observed for 1. Further comparison of the ¹³C spectra of complexes 1, 2, and 4, which differ in the degree of methyl substitution at

the C4 carbon atom, reveals that the shift of the C4 carbon atom to higher frequency relative to free diene increases with increasing substitution at the C4 carbon atom in the order 4 ($\Delta\delta = 11.1$) < 1 ($\Delta\delta = 14.5$) < 2 ($\Delta\delta = 17.5$). This behavior may be indicative of increased donation from the uncomplexed to complexed C==C bond with increasing methyl substitution of the C4 carbon atom. Conversely, complexes 3 and 5, which possessed a C2 methyl group, displayed more pronounced shift of the C2 diene carbon atom to higher frequency ($\Delta\delta = -16.3$ for 3 and $\Delta\delta = -11.1$ for 5) than did the complexes lacking substitution at the C2 carbon atom. This behavior may suggest a more even distribution of partial positive charge between the C2 and C4 carbon atoms of complexes 3 and 5 relative to complexes lacking substitution at the diene C2 position.

Fluxional Behavior of Complexes 3–7. As was observed for 1,3-pentadiene complex 1, 2,4-dimethyl-1,3-pentadiene complex 3 displayed fluxional behavior consistent with intramolecular exchange of the prochiral C1=C2 π -faces. The ¹³C NMR spectrum of 3 at -90 °C displayed a pair of phosphorus-coupled doublets at δ 36.3 and 36.2 ($J_{CP} = 24$ Hz) corresponding to the quaternary carbon atoms of diastereotopic *tert*-butyl groups (Figure 6). As the temperature was raised, these resonances broadened and coalesced, forming a single phosphorus-coupled doublet at δ 36.8 ($J_{CP} = 24$ Hz) at -60 °C; this coalescence behavior was unaffected by the presence of free 2,4-dimethyl-1, 3-pentadiene (150 mM). These observations are consistent with racemization of 3 via intramolecular C=C bond exchange through *s*-*cis* and *s*-*trans* η^4 -diene transition states and intermediates, as was proposed for complex 1 (Scheme 2).

Complexes 4–7, which contain diene ligands composed of identically substituted C=C groups, displayed variable-temperature NMR behavior consistent with facile intramolecular exchange of the complexed and uncomplexed C=C bonds of the diene ligand. For example, the ¹H NMR spectrum of 1,3-butadiene complex 4 at -90 °C displayed six one-proton multiplets at



Figure 6. Temperature dependence of the quaternary *tert*-butyl 13 C NMR resonances of 3 from -90 to -60 °C in CD₂Cl₂.



Figure 7. Temperature dependence of the vinylic ¹H NMR resonances of 4 from -90 to 15 °C in CD₂Cl₂. The small multiplets at δ 6.3, 5.2, and 5.1 correspond to free 1,3-butadiene.

 δ 6.48 and 6.18, corresponding to the C2 and C3 vinylic protons, and at δ 5.66, 5.56, 4.11, and 3.93 corresponding to the C4 (higher frequency) and C1 (lower frequency) vinylic resonances (Figure 7). As the temperature was raised, the resonances corresponding to C2 and C3 protons broadened and coalesced at -60 °C to form a time-averaged multiplet at δ 6.40 at 15 °C. Over the same temperature range, the resonances corresponding to the C1 and C4 protons broadened and coalesced at -45 °C to form a two-proton multiplet at δ ~5.0 at 15 °C. Also worth noting was that significant broadening of the vinylic resonances of 4 occurred prior to detectable broadening of the vinylic resonances of residual 1,3-butadiene, arguing against an intermolecular pathway for the exchange. An energy barrier of ΔG_{214}^{\dagger} = 9.6 kcal mol⁻¹ for interconversion of the diene C=C bonds of 4 was obtained from line shape analysis of the C2/C3 diene resonances near the coalescence temperature ($\tau_c = -59$ °C).

The ¹H NMR spectrum of 2,3-dimethyl-1,3-butadiene complex **5** at -60 °C displayed a 1:1 ratio of three-proton singlets at δ 2.25 and 1.73 corresponding to the diene methyl protons and a 1:1:1:1 ratio of one-proton resonances at δ 5.65, 5.48, 3.99, and 3.64 corresponding to the C4 (higher frequency) and C1 (lower frequency) vinylic protons (Figure 8). As the temperature was raised, the diene methyl resonances broadened and coalesced at -12 °C, forming a broad singlet ($\nu_{1/2} = 19$ Hz) at 2.04 at 20 °C. Over the same temperature range, the vinylic resonances



Figure 8. Temperature dependence of the vinylic (left column) and diene methyl (right column) ¹H NMR resonances of 5 from -60 to 20 °C. Resonances at δ 5.0 and 1.88 correspond to free diene, and the resonance at $\delta \sim 1.65$ corresponds to water. Vertical and horizontal scales are not consistent between the two sets of spectra.

broadened and coalesced, forming a broad four-proton multiplet at $\delta \sim 4.8$ at 20 °C. As was the case with 4, significant broadening of the vinylic and diene methyl resonances of 5 occurred prior to detectable broadening of the resonances of residual 2,3-dimethyl-1,3-butadiene, arguing against an intermolecular pathway for the exchange. An energy barrier of $\Delta G^{+}_{261K} = 11.9$ kcal mol⁻¹ for the diene C==C bonds of 5 was determined from line shape analysis of the diene methyl resonances at the coalescence temperature ($\tau_{c} = -12$ °C).

The ¹H NMR spectrum of 1,3-cyclohexadiene complex 6 at -85 °C displayed a 1:1:1:1 ratio of broad one-proton singlets at δ 6.18, 6.01, 5.59, and 5.13, corresponding to the H4, H3, H2, and H1 vinyl protons, respectively. As the temperature was raised, the H2/H3 pair of vinylic resonances at δ 6.01 and 5.59 broadened and coalesced at ca. -40 °C, forming a broad singlet at δ 5.89 at 0 °C. Over the same temperature range, the H1/H4 pair of vinylic resonances at δ 6.18 and 5.13 broadened and coalesced at ca. -30 °C, forming a broad singlet at \sim 5.7 at 0 °C (Figure 9). An energy barrier of $\Delta G^{\dagger}_{233K} = 10.4 \text{ kcal mol}^{-1}$ for exchange of the complexed and uncomplexed C=C bonds of 6 was determined from line shape analysis of the H2/H3 vinylic resonances near the coalescence point ($\tau_c = -40$ °C). Worth noting is the 1:1 pair of mutiplets at δ 2.46 and 2.32 ($\Delta v = 71$ Hz) in the fast-exchange $(0 \degree C)$ spectrum of 6, corresponding to the time-averaged C5/C6 protons positioned either *cis* or *trans* to the gold phosphine group (Figure 9). The presence of chemically inequivalent cis and trans C5/C6 protons establishes that the interconversion of complexed and uncomplexed C=C bonds of the 1,3-cyclohexadiene ligand of 6 occurs without concomitant exchange of the two faces of the 1,3-cyclohexadiene ligand. Because an intermolecular pathway for exchange of the complexed and uncomplexed C=C bonds of the 1,3-cyclohexadiene ligand of 6 would also interconvert the *cis*-C5/C6 and *trans*-C5/ C6 protons, we can safely rule out an intermolecular pathway for exchange of the complexed and uncomplexed C=C bonds of the 1,3-cyclohexadiene ligand of 6.

The ¹H NMR spectrum of 1,4-cyclohexadiene compound 7 at -70 °C displayed a 1:1 ratio of resonances at δ 5.57 and 5.71 corresponding to the vinylic protons of the complexed and uncomplexed C=C bond of the diene, respectively (Figure 10).



Figure 9. Temperature dependence of the vinylic (left column) and allylic (right column) ¹H NMR resonances of **6** from -85 to 0 °C in CD₂Cl₂. The resonance indicated with an "×" corresponds to an impurity. Vertical and horizontal scales are not consistent between the two sets of spectra.



Figure 10. Temperature dependence of the vinylic 1 H NMR resonances of 7 from -70 to -20 °C in CD₂Cl₂.

As the temperature was raised, the vinylic resonances broadened and coalesced at -45 °C, forming a single resonance at δ 5.7 at -10 °C. An energy barrier of $\Delta G^{\dagger}_{233} = 10.9$ kcal mol⁻¹ for exchange of the complexed and uncomplexed C=C bonds of 7 was determined from line shape analysis of the -45 °C spectrum. The ¹H NMR spectrum of 7 at -70 °C also displayed a fourproton multiplet at δ 2.85 corresponding to the allylic protons, which shifted slightly to higher frequency with increasing temperature, but remained otherwise unchanged over the temperature range -70 to -20 °C. As was the case with 1,3-cyclohexadiene complex 6, this observation argues against an intermolecular process for C=C bond exchange in 7 that would equilibrate the *cis* and *trans* allylic protons, leading to collapse of the allylic multiplet.

Several points are worth noting regarding the intramolecular exchange of the complexed and uncomplexed C=C bonds of the diene ligands of complexes 3–7. The energy barriers for exchange of complexed and uncomplexed C=C bonds for complexes 4–7 fall in the range $\Delta G^{\dagger} = 9.6-11.9$ kcal mol⁻¹. Butadiene complex 4 displayed the lowest barrier for exchange

Table 2. Line-Broadening Data and Observed Rate Constants (k_{obs}) for the Exchange of the 2,4-Dimethyl-1,3-pentadiene Ligand of 3 ([3] = 161 mM) with Free 2,4-Dimethyl-1,3-pentadiene in CD₂Cl₂ at 25 °C

| [2,4-dimethyl-1, 3-pentadiene] (M) | $\Delta u_{1/2}$ (Hz) | $\Delta v_{1/2(\text{excess})}$ (Hz) | $k_{ m obs} ({ m s}^{-1})$ |
|---------------------------------------|------------------------|--------------------------------------|-----------------------------|
| 0 | 6.9 | 0 | 0 |
| 0.09 | 11.0 | 4.0 | 12.7 |
| 0.14 | 13.7 | 6.8 | 21.3 |
| 0.18 | 15.8 | 8.9 | 27.9 |
| 0.22 | 17.9 | 10.9 | 34.3 |
| 0.25 | 19.2 | 12.3 | 38.5 |
| | | | |

 $(\Delta G_{233}^{\dagger} = 9.6 \text{ kcal mol}^{-1})$, while the 2,3-dimethyl-1,3-butadiene complex **5** displayed the highest barrier for exchange $(\Delta G_{261}^{\dagger} =$ 11.9 kcal mol⁻¹). Although we cannot rule out ground-state destabilization of 4 relative to 5 as the origin of these differences (see below), the higher energy barrier for exchange in the case of 5 presumably reflects increased steric destabilization of the transition state for formation of the three-coordinate, η^4 -diene intermediate. In the case of complexes 4 and 5, exchange of the complexed and uncomplexed C=C bonds of the diene ligand though either s-cis or s-trans η^4 -diene intermediates and transition states fully accounts for the observed fluxional behavior. Of course in the case of 1,3-cyclohexadiene complex 6, exchange must occur solely though s-cis η^4 -diene intermediates and transition states. In comparison, interconversion of the diastereotopic tert-butyl groups of 3 requires C=C bond exchange through both s-cis and s-trans η^4 -diene intermediates and transition states, as was proposed for complex 1. Although we were unable to obtain satisfactory simulations of the temperaturedependent ¹³C NMR spectra of complexes 1 and 3, the facile racemization of 1 and 3 suggests that both the *s*-*cis* and *s*-*trans* η^4 diene intermediates and transition states are easily accessible. Furthermore, the similar energy barriers observed for C=C bond exchange of 1,3-cyclohexadiene complex 6 and 1,4-cyclohexadiene complex 7 further suggest that the stability of the threecoordinate intermediates is only modestly sensitive to the geometry of the two alkene ligands and also that conjugation plays no significant role in the energetics of C=C bond exchange.

Kinetics of Intermolecular Diene Exchange with 3. All of our observations regarding the exchange of complexed and uncomplexed C=C bonds of diene complexes 1 and 3-7 argue against intermolecular pathways for C=C bond exchange. To independently determine the rate of intermolecular diene exchange, we studied the kinetics of 2,4-dimethyl-1,3-butadiene exchange with 3 as a function of [2,4-dimethyl-1,3-butadiene] in CD_2Cl_2 at 25 °C employing ¹H NMR line-broadening techniques.³⁷ Addition of 2,4-dimethyl-1,3-butadiene (93 mM) to a solution of 3 (160 mM) in CD₂Cl₂ at 25 °C led to excess line broadening of the C3 vinylic proton resonance at δ 5.74 of $\Delta v_{1/2}$ (excess) = 4.0 Hz, which corresponds to a first-order rate constant for exchange of $k_{obs} = \pi [\Delta v_{1/2}(excess)] = 12.7 \text{ s}^{-1}$ (Table 2). A plot of k_{obs} versus [2,4-dimethyl-1,3-butadiene] over the concentration range 0.093-0.25 M was linear, with a second-order rate constant for 2,4-dimethyl-1,3-butadiene exchange of $k_{\text{ex}} = 169 \pm 1 \text{ M}^{-1} \text{ s}^{-1} (\Delta G_{298}^{\dagger} = 14.40 \pm 0.01 \text{ kcal mol}^{-1};$ Figure 11). These data support an associative pathway for intermolecular diene exchange through the cationic, three-coordinate



Figure 11. Plot of k_{obs} versus [2,4-dimethyl-1,3-butadiene] for the intermolecular exchange of the 2,4-dimethyl-1,3-butadiene ligand of 3 ([3] = 160 mM) with free 2,4-dimethyl-1,3-butadiene from 93 to 245 mM at 25 °C in CD₂Cl₂.

bis(η^2 -diene) intermediate {[P(t-Bu)_{20}-biphenyl]Au[η^2 -H₂C= C(Me)C(H)=CMe₂]₂}+SbF₆⁻. As expected, the energy barrier for intermolecular diene exchange is considerably higher than was observed for the intramolecular exchange of complexed and uncomplexed C=C bonds in complexes 4–7 (ΔG^{\ddagger} = 9.6–11.9 kcal mol⁻¹). Also worth noting is that the rate of intermolecular exchange of 2,4-dimethyl-1,3-butadiene with 3 is only slightly lower that the rate of isobutylene exchange with [P(t-Bu)_{20}biphenyl]Au(η^2 -H₂C=CMe₂)}+SbF₆⁻ (9; $\Delta G^{\ddagger}_{298}$ = 15.0 ± 0.01 kcal mol⁻¹).¹²

Relative Binding Affinities of Dienes to Gold(I). We sought to determine the relative binding affinities of conjugated dienes to the cationic 12-electron gold fragment $[P(t-Bu)_2o$ biphenyl]Au⁺ both to determine the effect of diene substitution on the binding affinity of the dienes to gold(I) and to make direct comparisons among the binding affinities of conjugated dienes, aliphatic monoenes, and vinyl arenes. To this end, equilibrium constants for the displacement of isobutylene from 9 with several diene ligands were measured in CD_2Cl_2 at -70 °C employing ¹H NMR analysis (Table 3). The relative binding affinity of the dienes was only modestly sensitive to substitution and/or conjugation and decreased by a factor of ~ 13 in the order 1, 3-cyclohexadiene > 2,4-dimethyl-1,3-pentadiene > 1,4-cyclohexadiene > 2,3-dimethyl-1,3-butadiene > trans-1,3-pentadiene (Table 3). Furthermore, addition of butadiene to a solution of 9 in CD_2Cl_2 at -70 °C led to no detectable formation of butadiene complex 4, which suggests that 1,3-butadiene binds less tightly to gold than does trans-1,3-pentadiene.

We have previously shown that the binding affinities of *p*-substituted vinyl arenes to the cationic gold fragment $\left[P(t-t)\right]$ Bu)₂o-biphenyl]Au⁺ increased significantly with the increasing electron density of the aryl group.¹² Furthermore, aliphatic monoenes displayed significantly higher binding affinities to gold(I) than did vinyl arenes, presumably due to the electronwithdrawing nature of the sp^2 substituent of the vinyl arenes. For example, the relative binding affinity of isobutylene exceeded that of styrene by a factor of ~60 at $-60 \,^{\circ}\text{C}$ ($\Delta G = 1.73 \,\text{kcal mol}^{-1}$). In contrast, comparison of the relative binding affinities of 1,3cyclohexadiene ($K_{eq} = 1.21 \pm 0.05$) and 1,4-cyclohexadiene $(K_{\rm eq} = 0.60 \pm 0.2)$ points to conjugation as a nominally stabilizing feature of gold π -diene complexes. Also worth noting is that in the case of acyclic dienes that possessed an unsubstituted -CH=CH₂ group the relative binding affinity increased with increasing substitution at the uncomplexed C4 carbon atom

Table 3. Equilibrium Constants for Displacement of Isobutylene from $[P(t-Bu)_2 o$ -biphenyl]Au $(\eta^2$ -H₂C=CMe₂)]⁺-SbF₆⁻ (9) with Dienes in CD₂Cl₂ at -70 °C

$$\begin{array}{c|c} & \bigoplus \\ L & Au \\ Me \\ & Me \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\$$

| | diene | req | |
|---------------|------------------|---------------|--|
| 1,3-cyclohex | adiene | 1.21 ± 0.05 | |
| 2,4-dimethy | l-1,3-pentadiene | 0.93 ± 0.06 | |
| 1,4-cyclohex | adiene | 0.6 ± 0.2 | |
| 2,3-dimethy | l-1,3-butadiene | 0.14 ± 0.02 | |
| trans-1,3-per | ntadiene | 0.09 ± 0.01 | |
| trans-1,3-per | ntadiene | 0.09 ± 0.01 | |

in the order 1,3-butadiene < *trans*-1,3-pentadiene < 2,4-dimethyl-1,3-pentadiene. This observation further supports the bonding model of conjugated dienes to cationic gold(I) involving stabilization of the gold π -interaction through donation of electron density from the uncomplexed C=C bond to the complexed C=C bond of the diene ligand, as was also suggested by ¹³C NMR analysis of cationic gold η^2 -diene complexes.

CONCLUSION

We have synthesized seven cationic gold η^2 -diene complexes that contain the sterically hindered P(t-Bu)20-biphenyl ligand, and we have characterized these complexes by variable-temperature NMR spectroscopy and, in four cases, by X-ray crystallography. Both in solution and in the solid state, dienes that contain dissimilarly substituted C=C bonds bind to gold(I) selectively through the less substituted C=C bond. Analysis of the ¹³C NMR chemical shifts of the bound diene ligands and analysis of diene binding affinities points to stabilization of the gold π -diene interaction through donation of electron density from the uncomplexed C=C bond to the complexed C=C bond of the gold(I) π -diene complex. Variable-temperature NMR analysis established the fluxional behavior of cationic gold(I) π -diene complexes involving the facile ($\Delta G^{\dagger} = 9.6 - 11.9$ kcal mol⁻¹) intramolecular exchange of the complexed and uncomplexed C=C bonds of the diene ligand, presumably involving 16electron gold η^4 -diene intermediates and transition states.

EXPERIMENTAL SECTION

General Methods. Reactions were performed under a nitrogen atmosphere employing standard Schlenk and glovebox techniques unless specified otherwise. NMR spectra were obtained on a Varian spectrometer operating at 500 MHz for ¹H NMR, 125 MHz for ¹³C NMR, and 202 MHz for ³¹P NMR in CD₂Cl₂. Elemental analysis was performed by Complete Analysis Laboratories (Parsippany, NJ). Methylene chloride was purified by passage through columns of activated alumina under nitrogen. CDCl3 and CD2Cl2 were dried over CaH2 prior to use. {[P(t-Bu)₂o-biphenyl]Au[η^2 -H₂C=C(CH₃)₂]}+SbF₆⁻(9) was synthesized using a published procedure.¹² [P(t-Bu)₂o-biphenyl]AuCl, AgSbF₆, hexanes, 4-methylpentadiene, trans-1,3-pentadiene, 2,4-dimethyl-1,3-pentadiene, 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, 1, 3-cyclohexadiene, 1,4-cyclohexadiene, and isobutylene were purchased from major chemical suppliers and used as received. Line shape analysis was performed using WINDNMR-Pro.38 NMR probe temperatures were calibrated using a neat methanol thermometer.

Synthesis of Gold(I) η^2 -Diene Complexes. {[P(t-Bu)₂obiphenyl]Au[η^2 -(E)-H₂C=C(H)C(H)=C(H)Me]}+SbF_6^{-} (1). A mixture of $[P(t-Bu)_{2}o$ -biphenyl]AuCl (40 mg, 7.5 \times 10⁻² mmol), AgSbF₆ (26 mg, 7.5×10^{-2} mmol), and *trans*-1,3-pentadiene (51 mg, 0.75 mmol) was dissolved in CH₂Cl₂ (2 mL), forming a white suspension. The suspension was stirred in a sealed flask in the dark at room temperature for 6 h, then filtered through Celite. Volatile material was evaporated under vacuum to give 1 as a white solid (56 mg, 93%). ¹H NMR (30 $^{\circ}$ C): δ 7.92–7.86 (m, 1 H), 7.67–7.54 (m, 5 H), 7.32–7.18 (m, 3 H), 6.51 (ddd, J = 9.0, 10.5, 16.0 Hz, 1 H), 6.26 (qd, J = 7.0, 13.5 Hz, 1 H), 5.99 (ddd, *J* = 1.0, 10.5, 14.5 Hz, 1 H), 4.17 (d, *J* = 16.5 Hz, 1 H), 4.11 (d, *J* = 8.5 Hz, 1 H), 1.91 (dd, J = 1.0, 7.0 Hz, 3 H), 1.38 (d, J = 16.0 Hz, 18 H). ¹³C{¹H} NMR ($-80 \degree$ C): δ 147.4 (d, *J* = 13.9 Hz), 144.3, 142.6 (d, *J* = 7.4 Hz), 137.3, 133.5, 132.6 (d, J = 7.4 Hz), 131.0, 129.0, 129.0, 128.8, 128.3, 127.6 (d, J = 7.4 Hz), 127.3, 123.7 (d, J = 47.3 Hz), 90.6, 37.0 (d, J = 23.5 Hz, 36.9 (d, J = 23.6 Hz), 29.6 (br s), 18.4. ³¹P{¹H} NMR: δ 65.9 Anal. Calcd (found) for C25H35AuF6PSb: H, 4.32 (4.41); C, 37.46 (37.57).

 $\{[P(t-Bu)_2 o-biphenyl]Au[\eta^2-H_2 C=C(H)C(H)=CMe_2]\}^+SbF_6^-$ (**2**). A mixture of $[P(t-Bu)_2 o$ -biphenyl]AuCl (40 mg, 7.5 × 10⁻² mmol), AgSbF₆ (26 mg, 7.5 × 10^{-2} mmol), and 4-methyl-1,3-pentadiene (12 mg, 0.15 mmol) was dissolved in CH₂Cl₂ (2 mL), forming a white suspension. The suspension was stirred in a sealed flask in the dark at room temperature for 6 h, then filtered through a plug of Celite, eluting with CH₂Cl₂. The filtrate was concentrated to \sim 2 mL, diluted with hexanes (2 mL), and cooled at 4 °C overnight to form 1 (50 mg, 82%) as a white solid. ¹H NMR (25 °C): δ 7.95–7.91 (m, 1 H), 7.70–7.60 (m, 5 H), 7.35–7.22 (m, 3 H), 6.81 (ddd, *J* = 8.5, 11.5, 16.0 Hz, 1 H), 5.85 (d, J = 11.5 Hz, 1 H), 4.13 (d, J = 16.0 Hz, 1 H), 4.08 (d, J = 8.0 Hz, 1 H), 1.97 (s, 3 H), 1.95 (s, 3 H), 1.40 (d, J = 16.5 Hz, 18 H). ¹³C{¹H} NMR $(25 \text{ °C}): \delta 153.1, 148.8 \text{ (d, } J = 13.7 \text{ Hz}), 143.7 \text{ (d, } J = 6.3 \text{ Hz}), 134.9,$ 134.3, 133.7 (d, J = 7.5 Hz), 132.1, 130.0, 129.8, 128.4 (d, J = 6.2 Hz), 128.3, 124.7 (d, J = 46.3 Hz), 123.5, 90.6 (d, J = 15.0 Hz), 38.6 (d, J = 23.7 Hz), 30.8 (d, J = 7.5 Hz), 26.4, 19.5. ³¹P{¹H} NMR: δ 67.3. Anal. Calcd (found) for $C_{26}H_{37}AuF_6PSb$: H, 4.59 (4.70); C, 38.40 (38.42).

{[$P(t-Bu)_2o$ -biphenyl] $Au[\eta^2-H_2C=C(Me)C(H)=CMe_2]$ }+ SbF_6^- (**3**). Complex 3 was isolated as a white solid (62 mg, 100%) from the reaction of 2,4-dimethyl-1,3-pentadiene, [$P(t-Bu)_2o$ -biphenyl]AuCl, and AgSbF₆ employing a procedure similar to that used to synthesize 2. ¹H NMR (25 °C): δ 7.93–7.88 (m, 1 H), 7.65–7.55 (m, 5 H), 7.28–7.20 (m, 3 H), 5.04 (s, 1 H), 3.89 (d, J = 3.5 Hz, 1 H), 3.81 (d, J = 4.0 Hz, 1 H), 2.27 (s, 3 H), 1.96 (s, 3 H), 1.92 (s, 3 H), 1.37 (d, J = 16.5 Hz, 18 H). ¹³C{¹H} NMR (25 °C): δ 158.7, 149.4, 148.8 (d, J = 13.8 Hz), 143.7 (d, J = 7.5 Hz), 134.3 (d, J = 2.5 Hz), 133.8 (d, J = 7.5 Hz), 132.0 (d, J = 2.5 Hz), 130.0, 129.8, 128.3 (d, J = 7.5 Hz), 128.3, 125.1 (d, J = 5.0 Hz), 124.8 (d, J = 47.5 Hz), 91.7 (d, J = 16.3 Hz), 37.8 (d, J = 22.5 Hz), 30.7 (d, J = 6.2 Hz), 28.8, 28.0, 21.3. ³¹P{¹H</sup> NMR: δ 67.5. Anal. Calcd (found) for C₂₇H₃₉AuF₆PSb: H, 4.68 (4.75); C, 39.09 (39.20).

{ $[P(t-Bu)_2 o-biphenyl]Au[\eta^2-H_2 C=C(H)C(H)=CH_2]$ }+SbF₆ (**4**). Methylene chloride (2 mL) was added to a mixture of $[P(t-Bu)_2o$ biphenyl]AuCl (40 mg, 7.5×10^{-2} mmol) and AgSbF₆ (26 mg, $7.5 \times$ 10^{-2} mmol) under 1,3-butadiene atmosphere. 1,3-Butadiene was bubbled through the resulting suspension with stirring for 6 h at room temperature in the dark. The resulting suspension was filtered through Celite, and volatile material was evaporated under vacuum to give 4 (55 mg, 93%) as a white solid. ¹H NMR (-90 °C): δ 7.84-7.78 (m, 1 H), 7.59 - 7.52 (m, 5 H), 7.21 - 7.13 (m, 3 H), 6.48 (td, J = 10, 17.8 Hz, 1 H),6.18 (td, J = 10, 17.0 Hz, 1 H), 5.66 (d, J = 16.8 Hz, 1 H), 5.56 (d, J = 9.8 Hz, 1 H), 4.11 (d, J = 16.0 Hz, 1 H), 3.93 (br dd, J = 4.1, 7.2 Hz, 1 H), 1.26 (d, J = 16.7 Hz, 18 H). ¹³C{¹H} NMR (-90 °C): δ 147.2 (d, J =12.5 Hz), 142.5 (d, J = 7.5 Hz), 134.7 (d, J = 2.5 Hz), 133.5 (d, J = 2.5 Hz), 133.3, 132.4 (d, J = 7.5 Hz), 130.9 (d, J = 1.2 Hz), 129.1, 129.1, 128.9, 128.6, 128.5, 127.6 (d, *J* = 6.9 Hz), 127.3, 123.5 (d, *J* = 47.2 Hz), 94.9 (d, J = 12.6 Hz), 36.8 (d, J = 23.4 Hz), 36.5 (d, J = 23.6 Hz), 29.5.

 $^{31}P\{^{1}H\}$ NMR: δ 63.3. Anal. Calcd (found) for C_{24}H_{33}AuF_6PSb: H, 4.24 (4.33); C, 36.71 (36.67).

{[$P(t-Bu)_2o$ -*biphenyl*] $Au[\eta^2-H_2C=C(Me)C(Me)=CH_2$]}+ SbF_6^- (**5**). Complex **5** was isolated as a white solid (56 mg, 92%) from the reaction of 2,3-dimethyl-1,3-butadiene with [$P(t-Bu)_2o$ -biphenyl]AuCl and AgSbF₆ employing a procedure similar to that used to synthesize 1. ¹H NMR (-50 °C): δ 7.90–7.85 (m, 1 H), 7.67–7.58 (m, 5 H), 7.26–7.20 (m, 3 H), 5.65 (s, 1 H), 5.48 (s, 1 H), 3.99 (br d, J = 3.5 Hz, 1 H), 3.64 (br d, J = 4.0 Hz, 1 H), 2.25 (s, 3 H), 1.74 (s, 3 H), 1.36 (d, J = 16.5 Hz, 9 H), 1.25 (d, J = 17.0 Hz, 9 H). ¹³C{¹H} NMR (-60 °C): δ 154.7, 147.6 (d, J = 15.0 Hz), 143.1 (d, J = 7.5 Hz), 140.2, 133.7, 132.9 (d, J = 6.3 Hz), 131.3, 129.5, 129.4, 129.3, 128.9, 127.8 (d, J = 7.5 Hz), 127.7, 124.2, 123.9 (d, J = 47.5 Hz), 91.9 (d, J = 15.0 Hz), 36.4 (d, J = 23.7 Hz), 36.2 (d, J = 23.7 Hz), 30.2 (d, J = 5.0 Hz), 29.5 (d, J = 6.2 Hz), 24.0, 20.1. ³¹P{¹H} NMR (-60 °C): δ 63.5. Anal. Calcd (found) for C₂₆H₃₇AuF₆PSb: H, 4.59 (4.52); C, 38.40 (38.46).

{[$P(t-Bu)_2o$ -biphenyl] $Au[\eta^2 - C(H) = C(H)C(H) = C(H)CH_2CH_2$ } + SbF_6^- (**6**). Complex **6** was isolated as a white solid (61 mg, 100%) from the reaction of 1,3-cyclohexadiene with [$P(t-Bu)_2o$ -biphenyl]AuCl and AgSbF₆ following the procedure used to synthesize **1**. ¹H NMR ($-70 \,^{\circ}$ C): δ 7.86–7.79 (m, 1 H), 7.61–7.52 (m, 5 H), 7.26–7.18 (m, 3 H), 6.18 (br s, 1 H), 6.01 (br s, 1 H), 5.59 (br s, 1 H), 5.13 (br s, 1 H), 2.46–2.31 (m, 3 H), 2.21–2.08 (m, 1 H), 1.32 (d, J = 16.5 Hz, 9 H), 1.28 (d, J = 16.5 Hz, 9 H). ¹³C{¹H} NMR ($-70 \,^{\circ}$ C): δ 147.4 (d, J = 13.2 Hz), 142.6 (d, J = 6.5 Hz), 136.4, 133.5, 132.5 (d, J = 7.2 Hz), 131.0, 129.3, 129.1, 128.7, 128.5, 127.5 (d, J = 6.6 Hz), 127.2, 123.4,123.0 (d, J = 5.0 Hz), 121.1, 117.4 (d, J = 6.2 Hz), 114.6 (d, J = 8.3 Hz), 37.4 (d, J = 24.0 Hz), 37.2 (d, J = 23.8 Hz), 29.8 (d, J = 15.2 Hz), 24.4, 21.7. ³¹P{¹H} NMR ($-70 \,^{\circ}$ C): δ 61.9. Anal. Calcd (found) for C₂₆H₃₅AuF₆PSb: H, 4.35 (4.43); C, 38.49 (38.44).

{[$P(t-Bu)_2o$ -*biphenyl*] $Au[\eta^2-C(H)=C(H)CH_2C(H)=C(H)CH_2$ }+ SbF_6^- (**7**). Complex 7 was isolated as a white solid (61 mg, 93%) from the reaction of 1,4-cyclohexadiene with [$P(t-Bu)_2o$ -biphenyl]AuCl and AgSbF₆ employing a procedure similar to that used to synthesize 1. ¹H NMR ($-60 \,^{\circ}$ C): δ 7.86–7.79 (m, 1 H), 7.62–7.52 (m, 5 H), 7.25–7.22 (m, 1 H), 7.21–7.14 (m, 2 H), 5.71 (s, 2 H), 5.58 (s, 2 H), 2.95–2.76 (m, 1 H), 1.31 (d, J = 17.0 Hz, 18 H). ¹³C{¹H} NMR ($-85 \,^{\circ}$ C): δ 147.4 (d, J = 13.0 Hz), 142.5 (d, J = 7.0 Hz), 133.4 (d, J = 3.0 Hz), 132.5 (d, J = 7.5 Hz), 131.0, 129.2, 128.5, 127.5 (d, J = 6.4 Hz), 127.2, 123.4, 122.9 (d, J = 47.3 Hz), 120.7 (d, J = 6.9 Hz), 36.9 (d, J = 24.1 Hz), 29.8, 27.0. ³¹P{¹H} NMR ($-60 \,^{\circ}$ C): δ 62.2. Anal. Calcd (found) for C₂₆H₃₅AuF₆PSb: H, 4.32 (4.35); C, 38.40 (38.49).

X-ray Crystal Structure Determinations. Crystals of 1, 2, 4, and 7 were obtained from slow diffusion of hexanes into CH_2Cl_2 solutions of the respective complexes at 4 °C. The crystals were mounted on a Mitegen polyimide micromount with a small amount of Paratone N oil. Diffraction data were obtained with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) on a Bruker-Nonius Kappa Axis X8 Apex2 diffractometer at 110 K. Crystallographic data for complexes 1, 2, 4, and 7 are collected in Table 4. The data collection strategy employed ω and φ scans that collected data up to 2 θ . The frame integration was performed using SAINT.³⁹ The resulting raw data were scaled and absorption corrected using a multiscan averaging of symmetry equivalent data using SADABS.⁴⁰

The structures of 1, 4, and 7 were solved by direct methods using the XS program;⁴¹ the structure of complex 2 was solved by direct methods using the SIR92 program.⁴² All non-hydrogen atoms were obtained from the initial solution. The hydrogen atoms were introduced at idealized positions and were allowed to ride on the parent atom. The structural models were fit to the data using full matrix least-squares based on F^2 . The calculated structure factors included corrections for anomalous dispersion from the usual tabulation. The structures were refined using the XL program from SHELXTL;⁴³ graphic plots were produced using the NRCVAX crystallographic program suite.

| | 1 | 2 | 4 | 7 |
|---------------------------------------------|-------------------------------|------------------------------------------------------|------------------------------------------------------|------------------------------------------------------|
| empirical formula | C25.50H35AuClF6PSb | C ₂₆ H ₃₇ AuF ₆ PSb | C ₂₄ H ₃₃ AuF ₆ PSb | C ₂₆ H ₃₅ AuF ₆ PSb |
| fw | 840.67 | 813.24 | 785.19 | 811.23 |
| cryst size (mm ³) | $0.31\times0.20\times0.07$ | $0.32\times0.18\times0.06$ | $0.37\times0.29\times0.28$ | $0.16\times0.14\times0.11$ |
| color and habit | colorless prism | colorless prism | colorless prism | colorless plate |
| $T(\mathbf{K})$ | 110(2) | 110(2) | 110(2) | 110(2) |
| λ (Å) | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| cryst syst | monoclinic | orthorhombic | triclinic | monoclinic |
| space group | P2(1)/n | $Pca2_1$ | $P\overline{1}$ | $P2_{1}/n$ |
| unit cell dimens | a = 10.488(2) Å | a = 12.7007(4) Å | a = 9.4763(8 Å) | a = 9.9305(6) Å |
| | b = 17.861(4) Å | b = 11.9861(4) Å | b = 9.8824(8) Å | b = 24.7210(15) Å |
| | c = 15.443(3) Å | c = 18.9847(6) Å | c = 14.0672(11) Å | c = 11.5076(7) Å |
| | $\beta = 93.948(10)^{\circ}$ | | $\alpha = 83.970(3)^{\circ}$ | $\beta = 94.593(3)^{\circ}$ |
| | | | $\beta = 87.373(4)^{\circ}$ | |
| | | | $\gamma = 81.222(4)^{\circ}$ | |
| $V(\text{\AA}^3)$ | 2886.0(10) | 2890.08(16) | 1294.14(18) | 2815.9(3) |
| Ζ | 4 | 4 | 2 | 4 |
| $D_{\rm calc} \left({\rm g/cm}^3\right)$ | 1.935 | 1.869 | 2.015 | 1.913 |
| $2\theta_{\max}$ (deg) | 56.66 | 72.58 | 86.78 | 68.88 |
| abs coeff (mm^{-1}) | 6.214 | 6.112 | 6.821 | 6.273 |
| total no. of reflns | 91845 | 98 369 | 73 102 | 67 039 |
| no. of unique reflns | 6678 | 12 497 | 15 686 | 11 764 |
| no. params refined/restraints | 6678/311 | 12 497/360 | 15 686/341 | 11 764/322 |
| F(000) | 1616 | 1568 | 752 | 1560 |
| goodness-of-fit on F^2 | 1.188 | 1.033 | 1.002 | 1.029 |
| final <i>R</i> indices $[I > 2\sigma(I)]$ | $R_1 = 0.0265, wR_2 = 0.0595$ | $R_1 = 0.0364, wR_2 = 0.0722$ | $R_1=0.0260,wR_2=0.0604$ | $R_1 = 0.0463, wR_2 = 0.1033$ |
| R indices (all data) | $R_1 = 0.0346, wR_2 = 0.0619$ | $R_1 = 0.0624, wR_2 = 0.0848$ | $R_1 = 0.0312, wR_2 = 0.0619$ | $R_1 = 0.0942, wR_2 = 0.1172$ |
| max., min. $\Delta ho~({ m e}/{ m \AA}^3)$ | -2.044, 1.907 | -0.710, 1.857 | -2.359, 4.902 | -1.264, 2.295 |
| | | | | |

 Table 4. Crystal Data and Structure Refinement for Complexes 1, 2, 4, and 7

The 4-methyl-1,3-pentadiene ligand of complex **2** exhibited an orientational disorder. Atoms C2 and C5 occupied single positions, while atoms C1, C3, C4, and C6 occupied a second set of sites denoted as C1', C3', C4', and C6', respectively. The occupancies for the orientations were refined and normalized to 0.574(11) and 0.426(11) for the unprimed and primed sites respectively. The 1,3-butadiene ligand of **4** was likewise disordered over two orientations. The refined occupancy for the major component was 0.643(8).

Kinetics of Intramolecular C=C Bond Exchange. An NMR tube containing a solution of 4 (0.55 mg, 0.070 mmol) in CD₂Cl₂ (0.5 mL) was placed in the probe of an NMR spectrometer precooled at -90 °C, allowed to equilibrate for 10 min, and analyzed by ¹H NMR spectroscopy. The solution was warmed incrementally, equilibrated at -80, -70, -60, -59, -45, -30, -15, and 15 °C, and analyzed at each temperature by ¹H NMR spectroscopy. Simulation of the portion of the ¹H NMR spectrum containing the C2/C3 vinylic resonances $(\delta 6.1-6.6)$ at -59 °C employing the parameters $\Delta \omega = 144.9$ Hz, $\omega_a =$ 5 Hz, $\omega_{\rm b}$ = 4 Hz, $J_{\rm AB}$ = 10.0 Hz, $J_{\rm Atrans}$ = 17.8, $J_{\rm Acis}$ = 8.8 Hz, $J_{\rm Bcis}$ = 10.2 Hz, $J_{\text{Btrans}} = 17.0$ Hz gave a best fit with an exchange rate of $k_{\text{ex}} = 701$ s⁻¹ $(\Delta G_{214}^{\dagger} = 9.6 \text{ kcal mol}^{-1}; \text{ Figure S7})$. Peak separations $(\Delta \omega)$ were obtained directly from the -90 °C ¹H NMR spectrum of 4; coupling constants (J) were obtained from the $-90 \degree C$ ¹H NMR spectrum of 4 and then varied within ± 0.2 Hz to best reproduce the slow-exchange spectrum. Natural peak widths (ω) were estimated by averaging the peak width at half-height of the outer lines of the respective multiplets. The energy barriers for interconversion of the diene C=C bonds of complexes 5-7 were determined though similar analyses. Comparisons of experimental and simulated ¹H NMR spectra are included as Figures S7-S10 in the Supporting Information.

Kinetics of Intermolecular Diene Exchange with 3. An NMR tube capped with a rubber septum that contained a solution of 3 (59 mg, 0.072 mmol) and 1,3-dimethoxybenzene (0.018 mmol, 2.4 μ L, internal standard) in CD₂Cl₂ (0.445 mL) was placed in the probe of an NMR spectrometer maintained at 298 K. Analysis of the singlet at δ 5.74 corresponding to the C3 proton of the 2,4-dimethyl-1,3-pentadiene ligand of 3 in the ¹H NMR spectrum gave a peak width at half-height of $\Delta v_{1/2}$ = 6.9 Hz (Table 2). The tube was removed from the probe, and 2,4-dimethyl-1,3-pentadiene was added via syringe. The tube was inverted several times, returned to the probe, and allowed to equilibrate for 10 min. The concentration of free 2,4-dimethyl-1,3-pentadiene was determined as 0.09 M by integration of the C3 proton resonance of free 2,4-dimethyl-1,3-pentadiene at δ 5.65 relative to the multiplet at δ 6.48 corresponding to the C4, C5, and C6 aryl protons of 1,3-dimethoxybenzene. The peak width at half-height for the singlet at δ 5.74 was $\Delta v_{1/2} = 11.0$ Hz, corresponding to an excess broadening of $\Delta v_{1/2(\text{excess})} =$ 4.0 Hz (Table 2). Using this value, the rate of exchange of the diene ligand with 3 was determined through application of the slow exchange approximation to be $k_{obs} = \pi(\Delta v_{1/2(excess)}) = 12.7 \text{ s}^{-1}$. The first-order rate constant for diene exchange with 3 was determined in a similar manner at [2,4-dimethyl-1,3-butadiene] = 0.14, 0.18, 0.22, and 0.25 M (Table 2). The second-order rate constant for the rate of exchange of the diene ligand of 3 was determined from the slope of a plot of $k_{\rm obs}$ versus [2,4-dimethyl-1,3-butadiene] where $k_{ex} = 169 \pm 1 \text{ M}^{-1} \text{ s}^{-1} (\Delta G^{\ddagger} = 14.40 \text{ m}^{-1} \text{ s}^{-1})$ \pm 0.01 kcal mol⁻¹) (Table 2, Figure 11).

Determination of Diene Binding Constants. 2,3-Dimethyl-1,3-butadiene (2.4 mg, 0.029 mmol) was added via syringe to a CD₂Cl₂ solution of {[P(*t*-Bu)₂*o*-biphenyl]Au(η^2 -H₂C=CMe₂)}⁺SbF₆⁻ (9; 20 mg, 0.029 mmol) in an NMR tube sealed with a rubber septum. The contents

of the tube were thoroughly mixed, placed in the probe of an NMR spectrometer precooled at -70 °C, and maintained at this temperature for 10 min. The relative concentrations of 9, free isobutylene, 5, and free 2,3-dimethyl-1,3-butadiene were measured by integrating the resonances corresponding to the vinyl protons of bound (δ 3.73) and free (δ 4.59) isobutylene and the vinyl protons of bound (δ 5.60, 5.44, 3.95, 3.52) and free (δ 5.01, 4.95) 2,3-dimethyl-1,3-butadiene. An equilibrium constant of $K_{eq} = ([5][isobutylene])/([9][2,3-dimethyl-1,3-butadiene]) =$ 0.13 ± 0.02 was determined as the average of two separate experiments (Table 3). To ensure that equilibrium was achieved under these conditions, a similar experiment was performed through addition of isobutylene (0.017 mmol) to a CD_2Cl_2 solution of 5 (0.025 mmol). An equilibrium constant of $K_{eq} = ([5][isobutylene])/([9][2,3-dimethyl-$ 1,3-butadiene]) = 0.12 ± 0.01 was determined, which is not significantly different from that obtained by treatment of 9 with 2,3-dimethyl-1, 3-butadiene. The relative binding affinities of 1,3-cyclohexadiene, 2, 4-dimethyl-1,3-pentadiene, 1,4-cyclohexadiene, and trans-1,3-pentadiene relative to isobutylene at -70 °C were determined employing procedures analogous to that used to determine the binding affinity of 2,3-dimethyl-1,3-butadiene (Table 3).

ASSOCIATED CONTENT

Supporting Information. X-ray crystallographic data, assignments of ¹³C and ¹H diene resonances of complexes 1-6, and plots of experimental and simulated ¹H NMR spectra used to determine energy barriers for interconversion of diene C=C bonds of complexes 4-7. This material is available free of charge via the Internet at http://pubs.acs.org.

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