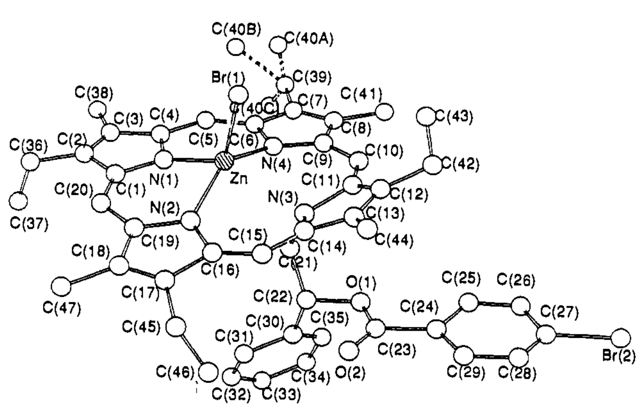

Figure 2. Molecular structure of the bromozinc complex of (*S*)-*N*-[(*R*)-2-(4′-bromobenzoyloxy)-2-phenylethyl]etioporphyrin I ((*R*)-**5b**-[FI]). Selected distances (Å) and angles (degrees): Zn–N(1) 2.04(2), Zn–N(2) 2.08(2), Zn–N(3) 2.13(2), Zn–N(4) 2.13(2), Zn–Br(1) 2.39(2), N(3)–C(21) 1.47(3); Br(1)–Zn–N(1) 120.8(6), Br(1)–Zn–N(3) 98.1(6).

from (*R*)-styrene oxide, two elution peaks with different peak areas (ratio of 2:1 for (*R*)-**4a**-[FI]/(*R*)-**4a**-[FII]) were observed. A similar observation was made for (*S*)-**4a** derived from (*S*)-styrene oxide (peak area ratio of 1:2 for (*S*)-**4a**-[FI]/(*S*)-**4a**-[FII]), indicating the possible discrimination of the two enantiotopic faces of **1b** in the N-alkylation with chiral epoxides.

The circular dichroism (CD) profiles of the stereoisomers of the zinc complexes (**2b**) and (**4b**) are shown in Figure 1. The enantiomers **2b**-[FI] and **2b**-[FII] showed negative and positive CD bands, respectively, in the Soret region (426 nm, Figure 1), which were perfect mirror images of each other with $|[\theta]|$ of ca. 5000 deg·cm^2·dmol^{-1}. In contrast, the diastereoisomers of **4b** showed split Cotton effects with enhanced intensities (Figure 1), where the mirror-image spectral patterns for (*R*)-**4b**-[FI] and (*S*)-**4b**-[FII] ((*R*)-**4b**-[FII] and (*S*)-**4b**-[FI]) indicate that these are the enantiomeric pair. The splitting and enhancement of the CD are obviously due to the induced CD associated with the presence of a chiral, chromophoric N-substituent in proximity to the porphyrin chromophore. When (*R*)-**4b**-[FI] ((*R*)-**4b**-[FII]) was mixed with an equimolar amount of (*S*)-**4b**-[FI] ((*S*)-**4b**-[FII]) to cancel the contribution of the induced CD, the resulting spectrum was virtually identical to that of **2b**-[FI] (**2b**-[FII]) (Figure 1).

The X-ray diffraction analysis was successful on a single crystal of the bromozinc complex ((*R*)-**5b**-[FI]),[12] derived from the diastereoisomer (*R*)-**4b**-[FI] by esterification of the hydroxy group in the N-substituent with 4-bromobenzoyl chloride followed by axial ligand exchange with NaBr. The molecular structure (Figure 2) shows that the N-alkylated pyrrole ring is tilted by 29° from the reference plane of the three nonalkylated nitrogen atoms. When the molecule is viewed from the same side of the alkylated nitrogen atom, the methyl → ethyl sequence at the β-positions of every pyrrole unit is clockwise. Based on this molecular structure, the configurations of (*R*)-**4b**-[FI] and the other three diastereoisomers can be assigned as schematically shown in Figure 1. Thus, the isomers of free-base **4a** eluting first (**4a**-[FI]) and second (**4a**-[FII]) respectively take *S*- and *R*-configurations at the alkylated nitrogen atoms. When these stereochemical structures are correlated with the CD spectra of the mixtures (*R*)-**4b**-[FI] + (*S*)-**4b**-[FI] and (*R*)-**4b**-[FII] + (*S*)-**4b**-[FII] in Figure 1, it can be concluded that the chiral free-base *N*-alkyletioporphyrin I with an *S*-configuration at the alkylated nitrogen atom shows a negative CD band in the Soret region, while the antipode with *R*-configuration shows a positive CD band.

Further studies are in progress to establish the general rule for deducing the structure–circular dichroism relationship of a series of chiral porphyrins with asymmetric nitrogen atoms.

Supplementary Material Available: Listings of detailed synthetic procedures and spectral data for **2a**–**4a** and **2b**–**4b**, crystal data and experimental conditions, positional and thermal parameters for (*R*)-**5b**-[F1], and bond distances and angles (11 pages); observed and calculated structure factors for (*R*)-**5b**-[F1] (18 pages). Ordering information is given on any current masthead page.

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(12) Crystal data and structure determination: orthorhombic; $P2_12_12$; a = 28.933(6), b = 13.171(3), c = 13.942(3) Å; D_{calcd} = 1.158 g·cm^{-3}; Z = 4. Intensity data were collected on a Rigaku AFC-5R (rotating anode) diffractometer and refined by full-matrix least-squares techniques. Out of 8560 reflections observed, as few as 2488 satisfied $I > 3\sigma(I)$; thus only the heavier atoms were refined anisotropically. One of the ethyl groups was disordered. The final R, R_w, and GOF were 0.086, 0.116, and 3.89, respectively.

A Versatile Route to the β-Substituted π-Allyl Complexes via Addition to a Cationic η^3-Propargyl Complex of Platinum

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π-Allyl complexes constitute an important class of compounds in organometallic chemistry, and they are useful for organic synthesis.[1] Metal-activated allylic functionalization further increases the versatility of such complexes.[2] A recent study on the η^3-propargyl complex by Casey et al. showing that the central carbon of a (propargyl)rhenium complex is prone to nucleophilic addition, yielding the β-substituted metallacyclobutene,[3] prompts us to report our independent discovery of a cationic η^3-propargyl complex of Pt(II). The unique propargyl feature remarkably enhances its reactivity toward a wide spectrum of organic substrates, opening a convenient path to the β-substituted π-allyl derivatives. Thus our work contributes to remedy the paucity of methodology in the synthesis of β-substituted π-allyl complexes.

In a typical procedure, *trans*-$\mathrm{Pt}(\eta^1\text{-CH=C=CH}_2)(\mathrm{Br})(\mathrm{PPh}_3)_2$ (**1**) (460 mg) was reacted with an equimolar amount of $AgBF_4$ (118 mg, 1.1 equiv) in 7 mL of degassed CH_2Cl_2 at −30 °C, which instantaneously resulted in the formation of a novel cationic η^3-propargyl derivative $[\mathrm{Pt}(\eta^3\text{-CH}_2\mathrm{CCH})(\mathrm{PPh}_3)_2](\mathrm{BF}_4)$ (**2**).[4] After AgBr was removed by filtration, the addition of degassed hexane to the solution caused the crystallization of whitish-yellow product. The isolated yield of **2** was 80% (370 mg). In the solid state, **2** is stable under dry nitrogen but rapidly deteriorates in air. It also suffers slow thermal decomposition in solutions at 20 °C. In various NMR spectra,[5] all ^{1}H, ^{13}C, and ^{31}P resonances of **2** show coupling only to a single ^{195}Pt nucleus and to two ^{31}P nuclei, suggesting that **2** is a mononuclear species with the $\mathrm{Pt}(\eta^3\text{-C}_3\mathrm{H}_3)(\mathrm{PPh}_3)_2$ composition. In the ^{1}H-coupled ^{13}C NMR

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(2) (a) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

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(4) A relevant analogue of Mo was reported by Krivykh, V. V.; Taits, E. S.; Petrovskii, P. V.; Struchkov, Y. T.; Yanovskii, A. I. *Mendeleev Commun.* **1991**, 103.

(5) Selective spectral data for **2**: ^{31}P NMR ($CDCl_3$) δ 11.5 (J_{PP} = 20.0 Hz, $J_{P\text{-}Pt}$ = 4179 Hz), 13.0 (J_{PP} = 20 Hz, $J_{P\text{-}Pt}$ = 3810 Hz); ^{1}H NMR ($CDCl_3$) δ 2.91 (dd with ^{195}Pt satellites, 2 H, J_{HH} = 2.4 Hz, J_{PH} = 6.5 Hz, J_{PtH} = 30.8 Hz, CH_2), 4.60 (ddt with ^{195}Pt satellites, 1 H, J_{HH} = 2.4 Hz, J_{PH} = 1.4, 8.1 Hz, J_{PtH} = 27.2 Hz, C*H*), 7.1–7.5 (m, 36 H, phenyl H); ^{13}C NMR ($CDCl_3$, 268 K, 50.324 and 125.76 MHz) δ 51.9 (tdd with ^{195}Pt satellites, $^1J_{CH}$ = 171 Hz, J_{CP} = unresolved, 39 Hz, J_{CPt} = 105 Hz, *C*H_2CCH), 90.6 (ddd with ^{195}Pt satellites, $^1J_{CH}$ = 246 Hz, J_{CP} = 2.7, 49 Hz, J_{CPt} = 137 Hz, CH_2C*C*H), 101.4 (ddd with ^{195}Pt satellites, $^2J_{CH}$ = 29 Hz, J_{CP} = 2.7, 4.7 Hz, J_{CPt} = 58 Hz, CH_2*C*CH), 128–134 (d, phenyl carbons).

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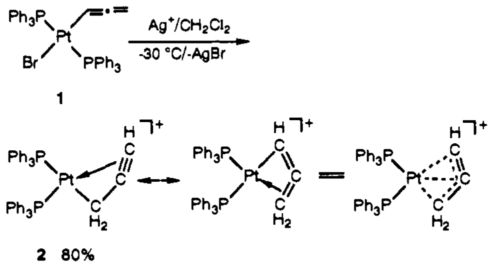
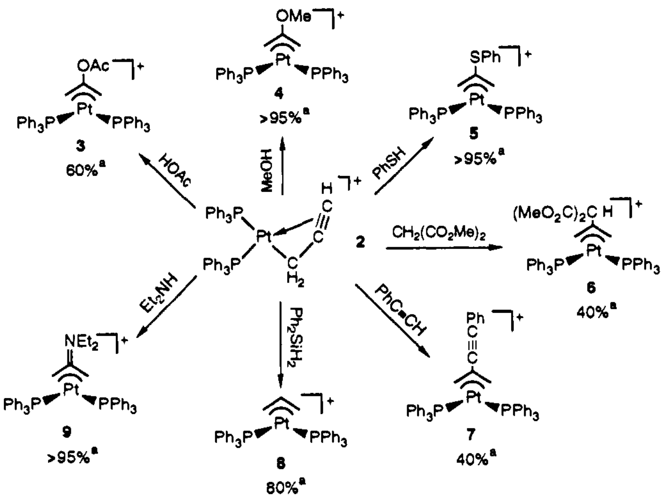
Scheme I



Scheme II



^{a}All product yields were estimated on the basis of ^{31}P NMR measurements.

spectrum of **2**, a doublet at δ 90.6 having $J_{CH} = 246$ Hz is assigned to the CH of the propargyl terminus and a triplet at δ 51.8 with $J_{CH} = 171$ Hz is assigned to the propargyl CH_2, the large coupling constant of which suggests the possibility of an η^3-allenyl resonance structure (Scheme I).[6] Such a highly strained η^3-propargyl feature also explains the unusually large values of J_{PtP} (3810 and 4179 Hz) and the unusually small values of $J_{PtC(terminal)}$ (105 and 137 Hz).[6-8]

Complex **2** readily undergoes an addition reaction with a wide range of hard and soft species including weak protic acids (HOAc, MeOH, and PhSH) and weak carbon acids ($H_2C(CO_2Me)_2$ and PhC≡CH) to generate β-substituted π-allyl complexes $[Pt(\eta^3\text{-}CH_2C(Y)CH_2)(PPh_3)_2](BF_4)$ (Y = OAc, **3**; OMe, **4**; SPh, **5**; $CH(COOMe)_2$, **6**; C≡CPh, **7**). In the reaction of **2** with Ph_2SiH_2, only the simple allyl complex (Y = H, **8**) was obtained (Scheme II). While π-allyl products were characterized spectroscopically, the structure of **5** was confirmed by crystallography.[8] The analogous reaction of **2** with Et_2NH yielded platinum η^3-azatrimethylenemethane $[Pt(\eta^3\text{-}CH_2C(=NEt_2)CH_2)(PPh_3)_2](BF_4)$ (**9**) at a rate exceedingly faster than its formation from the reaction of **1** and the amine.[3b] Note that the other complexes (**3**–**8**) cannot be prepared directly from **1**. Exclusive addition of MeOH, PhSH, or Et_2NH to **2** was complete on mixing the reactants at 0 °C, judging from immediate NMR measurements. The reactions with other reagents are relatively slow.[9]

Although regioselective addition of nucleophiles to the propargyl complex has been known,[11] the reactivity of neutral malonate ester, phenylacetylene, and silane without the assistance of a base is unprecedented. The versatile bond-forming ability of the η^3-propargyl ligand activated by π-interaction with the cationic metal center suggests a rich chemistry. The reaction scope and mechanism of such transformations and application to organic synthesis are certainly worthy of further investigation.

Acknowledgment. We are grateful to the National Science Council, ROC, for financial support and to the Institute of Chemistry, Academia Sinica, Nangkang, for help in (500 MHz) NMR measurements. J.-T.C. thanks Professor T.-Y. Luh for helpful discussion. Stimulating comments and suggestions as to the structure of **2** and the possible reaction mechanisms from Professor Charles P. Casey, Department of Chemistry, University of Wisconsin, are gratefully acknowledged.

Supplementary Material Available: Experimental and characterization data for complexes **1**–**9** including two NMR spectra of **2** and crystal data and an ORTEP drawing of **5** (7 pages). Ordering information is given on any current masthead page.

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[6] For comparison: ^{1}H-coupled ^{13}C NMR data of $\{Pt[\eta^3\text{-}CH_2CHCH_2](PPh_3)_2\}(BF_4)$ (**8**) δ 69.9 (t, $J_{CH} = 161$ Hz, C_α); ^{31}P NMR δ 17.02 ($J_{P\text{-}Pt} = 3989$ Hz).

[7] The value of $J_{P\text{-}Pt}$ for a P trans to a Pt–C(σ) bond is ~2000 Hz; the value of J_{CPt} for a carbon of Pt–C(σ) bond is ~500 Hz.[1]

[8] Selected spectral data for $\{Pt[\eta^3\text{-}(CH_2C(SPh)CH_2)](PPh_3)_2\}(BF_4)$ (**5**): ^{31}P NMR ($CDCl_3$) δ 18.16 ($J_{P\text{-}Pt} = 3801$ Hz); ^{1}H NMR ($CDCl_3$) δ 3.13 (2 H, $J_{HH} = 3.4$ Hz, $J_{PH} = 8.4$ Hz, $J_{PtH} = 42.5$ Hz, H_{anti}), 3.26 (2 H, $J_{HH} = 3.4$ Hz, H_{syn}), 7.1–7.5 (m, phenyl H); ^{13}C NMR ($CDCl_3$) δ 63.0 (dd with ^{195}Pt satellites, $J_{PC} = 4.7$, 37 Hz, $J_{PtC} = 98$ Hz, C_α), 126–136 (phenyl carbons), 142.3 (t, $J_{PC} = 2.6$ Hz, C_β). Crystal data of $C_{45}H_{39}P_2SPtBF_4\cdot CH_2Cl_2$: $P\bar{1}$, $a = 11.285(3)$ Å, $b = 11.615(2)$ Å, $c = 17.946(2)$ Å, $\alpha = 106.57(1)°$, $\beta = 91.44(1)°$, $\gamma = 106.43(2)°$, $V = 2148.2(6)$ Å^3; Mo Kα radiation $\lambda = 0.7107$ Å, $Z = 2$, $\mu = 3.59$ mm^{-1}; 5620 total reflections, 4819 observed reflections ($I > 2.0\sigma(I)$), $R = 0.030$, $R_w = 0.025$.

[9] Noting that the overall reactions from **2** to **3**–**9** involve both protonation to a terminal carbon and nucleophilic addition to the central carbon of the propargyl ligand, the mechanism may comprise either (1) leading nucleophilic attack to the central carbon, yielding an intermediate of platinacyclobutene[4,10] followed by protonation, or (2) protonation first, resulting a π-allene complex which then adds a nucleophile to the central carbon.

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Concerning the Formation of Hydrogen in Nuclear Waste. Quantitative Generation of Hydrogen via a Cannizzaro Intermediate

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During the storage of certain nuclear waste, particularly mixtures containing complexing agents like EDTA and HEDTA in highly basic media, mixtures of gases containing large amounts of hydrogen are produced. In order to provide the foundation for control of this potentially dangerous situation, a fundamental understanding of the reactions responsible for the formation of hydrogen is crucial. Since it is known that the photolytic,[1] radiolytic,[2] and thermal[3] degradation of EDTA produces formaldehyde, it is reasonable to assume that formaldehyde is formed during the storage of nuclear waste, and that it could be an important intermediate in the generation of hydrogen. In a study

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