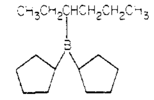
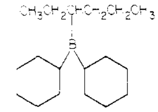
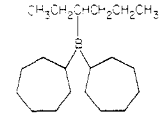
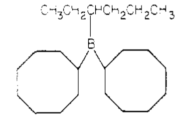
Table I. Thermal Isomerization[a] of *B*-(3-Hexyl)dicycloalkylboranes

organoborane	$t_{1/2}$,[b] s	time to reach equilibrium, h	% composition of hexanols of equilibrium		
			1-ol	2-ol	3-ol
	900	48	93	5	2
	300	48	97	2	1
	60	2	98	1	1
	9	1	99	1	0

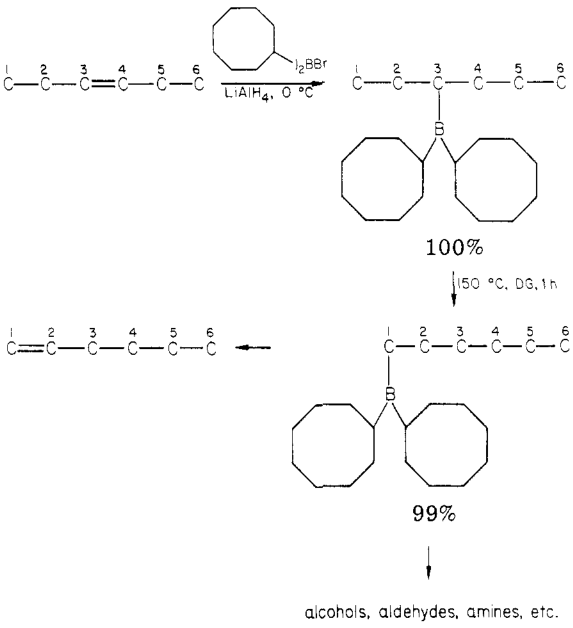
[a] All thermal isomerizations were done at 150 ± 2 °C in diglyme with 0% hydride excess. [b] $t_{1/2}$ was determined graphically from kinetic data obtained in each case.

the rate of isomerization and the equilibrium distribution increase in the same direction, consistent with the importance of a steric factor in both phenomena.

The following procedure is representative for the preparation of 3-hexyldicycloalkylboranes. Dicycloheptylbromoborane was first prepared by adding 1.2 mL of 8.3 M $BH_2Br{\cdot}SMe_2$ (neat liquid, 10 mmol) to 2.115 g of cycloheptene (22 mmol) in 5 mL of dry CH_2Cl_2 at 0 °C and then stirring the solution at 25 °C for 5 h. The completion of the reaction was checked by ^{11}B NMR. The solvent CH_2Cl_2 and excess olefin were then pumped off under vacuum, and the reaction mixture was dissolved in 5 mL of anhydrous ether. Next, 1.5 mL of *cis*-3-hexene (12 mmol) was added, followed by 2.6 mL of 0.98 M $LiAlH_4$ solution[3] in ether 2.5 mmol), and the reaction mixture was stirred at 0 °C for 12 h. The excess olefin and solvent ether were then pumped off under vacuum, and 10 mL of anhydrous pentane was added. Next, 2.6 mL of 3.9 M NaOMe (10 mmol) in methanol was added to precipitate aluminum bromide as aluminum methoxide, and then the supernatant liquid was carefully transferred into another flask. The precipitate was washed twice with 2 mL of pentane, and the washings were added to the already collected pentane solution. The pentane was subsequently evaporated, and the trialkylborane was distilled under very high vacuum (0.005-mmHg pressure). The pure 3-hexyldicycloheptylborane was then dissolved in 10 mL of dry diglyme, and the resulting mixture was isomerized at 150 ± 2 °C by using a thermowatch. The progress of the isomerization was checked at regular intervals of time by oxidizing 1-mL aliquots with alkaline hydrogen peroxide and analyzing the alcohols (extracted into ether) by GC. The standard conditions used for GC analysis were 10% Carbowax 1540 on Chromosorb W ($^1/_8$ in. × 12 ft) and isothermal analysis at 70 °C (Varian 1200 FID GC). A nitrogen atmosphere was maintained until the completion of oxidation.

Thus, the present exploratory study clearly brings out the influence of an important steric factor, namely, the ring size of the cycloalkyl substituents on the boron atom, on the rate and equilibrium of thermal isomerization of 3-hexyldicycloalkylboranes. It also enhances the scope of thermal isomerization for synthetic purposes (Scheme I).

Scheme I



We continue to explore the steric influences on the rate and equilibrium of thermal isomerization. Efforts are currently underway to develop dicycloalkylboranes from still higher membered rings, which we hope to be of utmost synthetic importance.

Coupling of Methylidyne and Carbonyl Ligands on Tungsten. Crystal Structure of $W(\eta^2\text{-}HC{\equiv}COAlCl_3)(CO)(PMe_3)_3Cl$

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Summary: $W(CH)(PMe_3)_4Cl$ reacts with carbon monoxide in the presence of AlX_3 (X = Me or Cl) to give complexes of the type $W(\eta^2\text{-}HC{\equiv}COAlX_3)(CO)(PMe_3)_3Cl$. Single crystals of $W(\eta^2\text{-}CH{\equiv}COAlCl_3)(CO)(PMe_3)_3Cl$ are monoclinic, space group $P2_1/c$, with a = 10.4197 (17) Å, b = 12.8965 (25) Å, c = 19.3194 (45) Å, β = 105.88 (2)°, V = 2497 (1) Å^3, and ρ(calcd) = 1.73 g cm^{-3} for Z = 4 and molecular weight 650.

Carbon–carbon bond formation via the reaction of surface-bound methylene or methylidyne groups with carbon monoxide might play a significant role in heterogeneous metal-catalyzed reductions of carbon monoxide with molecular hydrogen,[1] even though the latest theory

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[3] Brown, H. C.; Kulkarni, S. U. *J. Organomet. Chem.* 1981, *218*, 309.

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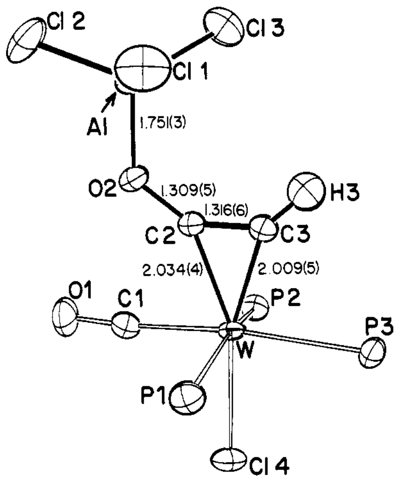

Figure 1. The structure of W(η^2-HC≡COAlCl$_3$)(CO)(PMe$_3$)$_3$Cl (ORTEP-II, 30% ellipsoids).

(a version of the original proposal by Fischer and Tropsch) is that the carbon–carbon bond is formed by migration of a surface alkyl to a surface alkylidene group.[2] Coupling of carbon monoxide with a methylene or methylidyne ligand is also a possible step in homogeneous systems in which carbon monoxide is reduced by molecular hydrogen. Since we recently reported the preparation and structures of W(CH)(Cl)(PMe$_3$)$_4$ along with the unusual aluminated derivatives W(CH·AlR$_3$)(Cl)(PMe$_3$)$_3$[3,4] and W(CAl$_2$Me$_4$Cl)(CH$_3$)(PMe$_3$)$_2$(η^2-C$_2$H$_4$),[5] we became interested in studying the reactions of such molecules with carbon monoxide. We report here the preparation and structure of the product of the reaction between W(CH)(Cl)(PMe$_3$)$_4$ and carbon monoxide in the presence of aluminum reagents.

W(CH)(Cl)L$_4$ (L = PMe$_3$) does not react cleanly with carbon monoxide (30 psi, 24 h, 25 °C). In the presence of AlMe$_3$, however, an orange-red crystalline product with the composition W(CH)(CO)$_2$(PMe$_3$)$_3$(Cl)(AlMe$_3$) can be isolated in 83% yield.[6] Its ^{13}C NMR spectrum showed three low-field resonances, two of which can be ascribed to carbonyl carbon atoms and the third to a methyne carbon atom with $J_{\mathrm{CH}} = 200$ Hz.[7] Its IR spectrum shows a CO stretch at 1960 cm^{-1} and one at 1615 cm^{-1}. An analogous AlCl$_3$ complex can be prepared by employing 2 equiv of AlCl$_3$ in chlorobenzene.[8] A crystal of "W(CH)(CO)$_2$(PMe$_3$)$_3$(Cl)(AlCl$_3$)" suitable for X-ray diffraction was obtained by recrystallization from a mixture of dichloromethane and toluene at −10 °C.

Crystals of "W(CH)(CO)$_2$(PMe$_3$)$_3$(Cl)(AlCl$_3$)" are monoclinic, space group $P2_1/c$, with a = 10.4197 (17) Å, b = 12.8965 (25) Å, c = 19.3194 (45) Å, β = 105.88 (2)°, V = 2497 (1) Å^3, and ρ(calcd) = 1.73 g cm^{-3} for Z = 4 and mol wt 650.0. Diffraction data were collected with a Syntex P2$_1$ four-circle automated diffractometer using a coupled θ(crystal)–2θ(counter) scan technique[9] and the structure was solved by standard Patterson, difference-Fourier and full-matrix least-squares refinement techniques. All atoms (including the 28 hydrogen atoms) were located and refined. The final discrepancy indices are R_F = 3.2% and R_{wF} 3.0% for all 4423 independent reflections with $4.0 < 2\theta < 50.0°$ (Mo Kα radiation; no reflections rejected).

The structure of the complex, which turns out to be W(η^2-HC≡COAlCl$_3$)(CO)(PMe$_3$)$_3$Cl, is shown in Figure 1. The complex results from coupling of carbonyl and methylidyne ligands, possibly accelerated by coordination of the Lewis acid to a carbonyl oxygen atom (see later). The essentially planar HCCOAl system is best regarded as a coordinated acetylene derivative rather than as a ketenoid derivative. The tungsten–carbon distances, W–C(2) = 2.034 (4) Å and W–C(3) = 2.009 (5) Å, are nearly equivalent. The acetylenic C(2)–C(3) distance of 1.316 (6) Å and the bending of the two acetylenic substituents away from the metal (∠C(3)–C(2)–O(2) = 143.5 (4)°; ∠C(2)–C(3)–H(3) = 137 (3)°) are consistent with values found in other structures in which the C≡C bond is substantially activated upon coordination.[10] The X-ray determined C(3)–H(3) distance of 1.05 (5) Å is reasonable.[11] Formation of the HCCOAlCl$_3$ ligand is consistent with the spectroscopic data, in particular the ν_{CO} stretch at 1615 cm^{-1} (the C(2)–O(3) bond is significantly longer than a typical carbonyl C–O bond) and the significant coupling of H(3) to C(2) (3.8 Hz) in the analogous product made by using ^{13}CO. The aluminum–oxygen bond (Al–O(2) = 1.751 (3) Å) is significantly shorter (and stronger) than the Al–O bond in molecules in which the AlX$_3$ group acts as a bridge between the oxygen atom and the metal (e.g., Al–O = 1.81 (1) Å in Mn(C(OAlBrBr$_2$)(CO)$_4$[12]).

The remainder of the structure is unexceptional. In the terminal carbonyl ligand, W–C(1) = 1.984 (4) Å, C(1)–O(1) = 1.150 (6) Å, and ∠W–C(1)–O(1) = 175.0 (4)°. The two mutually trans W–P distances are equivalent (W–P(1) = 2.519 (1) Å and W–P(2) = 2.523 (1) Å), while the third (trans to the CO ligand) is somewhat longer (W–P(3) =

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[1] (a) "Catalytic Activation of Carbon Monoxide"; Ford, P. C., Ed.; American Chemical Society: Washington, D.C., 1981; *ACS Symp Ser. No. 152.* (b) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479. (c) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61. (d) Henrici-Olivé, G.; Olivé, S. *Angew Chem., Int. Ed. Engl.* **1976**, *15*, 136. (e) Ponec, V. *Catal. Rev.—Sci. Eng.* **1978**, *18*, 151.

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[4] Churchill, M. R.; Rheingold, A. L.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 3392.

[5] Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 4119.

[6] W(CH)(Cl)(PMe$_3$)$_4$ (1.0 g, 1.9 mmol) was dissolved in toluene, and AlMe$_3$ (0.13 g, 1.9 mmol) was added at 25 °C. The mixture was stirred under 30 psi of CO at 25 °C for 2 days, and the solvent was removed in vacuo. The residue was dissolved in CH$_2$Cl$_2$, and the solution was filtered and concentrated to 4 mL. Pentane (3 mL) was added, and after the mixture was left standing at −10 °C for 1 day, 0.54 g of orange-red crystals was collected. A second crop of 0.21 g was obtained from the mother liquor by the same procedure; total yield 0.75 g (83%). Anal. Calcd for WC$_{15}$H$_{37}$AlClO$_2$P$_3$: C, 30.58; H, 6.29. Found: C, 30.12; H, 6.18.

[7] ^{1}H NMR (CD$_2$Cl$_2$, 250 MHz, 295 K) 12.75 (br d, 1, J_{HP} = 18.9 Hz, W(C*H*COAlMe$_3$)), 1.70 (d, 9, J_{HP} = 6.7 Hz, PMe$_3$), 1.36 (t, 18, J_{HP} = 3.7 Hz, PMe$_3$), −1.0 ppm (br s, 9, AlMe$_3$). ^{13}C NMR (CD$_2$Cl$_2$, 62.8 MHz, 295 K): 226.3 (s, W-CO), 215.2 (d, J_{CP} = 34.9 Hz, W-CO), 196.2 (br d, J_{CH} = 200 Hz, W(*C*HCOAlMe$_3$)), 18.3 (br m, J_{CP} = 5.8 Hz, PMe$_3$), 18.6 (d, J_{CP} = 17.4 Hz, PMe$_3$), −7.8 ppm (br q, J_{CH} = 110 Hz, AlMe$_3$). ^{31}P NMR (CH$_2$Cl$_2$, 36.2 MHz, 295 °C): −25.4 (d, J_{PP} = 19.5 Hz, PMe$_3$), −31.3 ppm (t, J_{PP} = 20.1 Hz, PMe$_3$). IR (Nujol, cm^{-1}): 1960, 1615.

[8] W(CH)(Cl)(PMe$_3$)$_4$ (2.0 g, 3.7 mmol) was dissolved in 10 mL of chlorobenzene, and AlCl$_3$ (1.0 g, 7.5 mmol) was added rapidly as a solid. The mixture was then stirred under 30 psi of carbon monoxide at 25 °C for 1 day. The resulting dark brown solution containing a light colored precipitate was filtered, and the insolubles were washed with 10 mL of acetonitrile at −10 °C. The orange-red insolubles were dissolved in dichloromethane, and the solution was filtered. The dichloromethane solution was concentrated to 3 mL and filtered to give 1.2 g of orange solid (50% yield). ^{1}H NMR (CD$_2$Cl$_2$, 250 MHz, 295 K): 12.1 (d, 1, J_{HP} = 12.5 Hz, WCHCOAlCl$_3$), 1.8 (d, 9, J_{HP} = 7.5 Hz, PMe$_3$), 1.4 ppm (t, 18, J_{HP} = 4.4 Hz, PMe$_3$). ^{13}C NMR (CD$_2$Cl$_2$, 62.8 MHz, 295 K): 230.8 (br s, W-CO), 213.5 (d, J_{CP} = 38.8 Hz, W-CO), 194.4 (d of d, J_{CH} = 202.5 Hz, J_{CP} = 22.2 Hz, W(CHCOAlCl$_3$)), 18.7 (br q, J_{CH} = 130.4 Hz, PMe$_3$), 18.4 ppm (q of d, J_{CH} = 130.4 Hz, J_{CP} = 16.7 Hz, PMe$_3$). ^{31}P NMR (CH$_2$Cl$_2$, 36.2 MHz, 295 K): −25.7 (d, J_{PP} = 19.5 Hz, J_{PW} = 264 Hz, PMe$_3$), −30.5 ppm (t, J_{PP} = 19.5 Hz, J_{PW} = 144 Hz, PMe$_3$). IR (Nujol, cm^{-1}): 1970, 1605. Λ (1.6×10^{-3} M, CH$_2$Cl$_2$) = 1.95 Ω^{-1} cm^{-1} M^{-1}.

[9] Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265.

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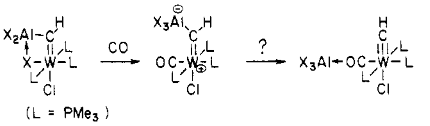
[11] Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

[12] Butts, S. B.; Strauss, S. H.; Holt, E. M.; Stimson, R. E.; Alcock, N. W.; Shriver, D. F. *J. Am. Chem. Soc.* **1980**, *102*, 5093.

2.571 (1) Å). Cis angles about the octahedral tungsten range from ∠P(2)–W–Cl (4) = 81.06 (4)° through ∠P(1)–W–Ac = 98.9°. (Ac represents the midpoint of the acetylenic C(2)–C(3) bond and the acetylene ligand is considered monodentate.)

One of the more interesting questions concerns the role of the aluminum reagent. Since $W(CH)(Cl)L_4$ reacts with AlX_3 reagents (2 equiv) to give $W(CH)(Cl)L_3(AlX_3)$ and Me_3PAlX_3,[3] it is reasonable to propose this as the first step, followed by coordination of CO in the position of the ligand bridging between Al and W (eq 1). The question then



(1)

reduces to whether the two carbon atoms couple at this point or later. Since activation of carbonyl ligands by interaction of the carbonyl oxygen atom with a Lewis acid is well documented,[13] it might seem more necessary for AlX_3 to activate the carbon monoxide toward coupling than the methylidyne ligand. On the other hand, it is also attractive to postulate that the two carbenoid ligands (CO and $C(H)(AlX_3)$) couple first and that AlX_3 (probably from outside the coordination sphere) subsequently coordinates to the carbonyl oxygen atom. In either case, AlX_3 plays an intimate role in the coupling reaction. Preliminary experiments suggest that removing $AlCl_3$ from $W(\eta^2\text{-}HC{\equiv}COAlCl_3)(CO)(PMe_3)_3Cl$ with a strong base (in order to generate $W(CH)(CO)(PMe_3)_3Cl$) is not facile.

Acknowledgment. This work was supported by the National Science Foundation through Grant CHE80-23446 (M.R.C.) and by the Director, Office of Basic Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy, under Contract DE-AC02-78ER04949-A002 (R.R.S.).

Supplementary Material Available: Positional parameters, anisotropic thermal parameters, and observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

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Photochemical Generation of Bis(triethylphosphine)platinum(0) and Synthesis of Ethylenebis(triethylphosphine)platinum(0)

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Summary: UV irradiation of the platinum(II) oxalate complex $Pt(PEt_3)_2(C_2O_4)$ in the presence of coordinating ligands L or oxidative addition substrates X-Y produces, respectively, $Pt(PEt_3)_2L_n$ (n = 1, 2) and $Pt(PEt_3)_2XY$, with release of two equivalents of CO_2. When L = ethylene, $Pt(PEt_3)_2(C_2H_4)$ can be prepared; its reactions are described.

Zerovalent, 14-electron complexes consisting of platinum and two tertiary phosphine ligands, PtL_2, are stable only if L is so sterically demanding that approach to the metal center is hindered.[1,2] The steric bulk of the ligands, however, attenuates the reactivity of these compounds. The crowded complex $Pt[P(t\text{-}Bu)_3)]_2$ does not react with dioxygen, molecular hydrogen, or methanol; as L becomes smaller [e.g., L = $P(t\text{-}Bu)_2Ph$, $P(c\text{-}Hx)_3$, $P(i\text{-}Pr)_3$], the reactivity of PtL_2 toward small molecules increases.[3,4] Relatively unhindered PtL_2 complexes, where L is a small phosphine ligand, have not been observed and should be highly reactive. For example, one phosphine can dissociate from $Pt(PEt_3)_4$ to give the 16-electron species $Pt(PEt_3)_3$, but further dissociation to produce spectroscopically observable quantities of $Pt(PEt_3)_2$ does not occur.[5-8] The oxalate complex $Pt(PPh_3)_2(C_2O_4)$ loses 2 equiv of carbon dioxide upon UV irradiation to produce platinum(0) compounds, presumably via $Pt(PPh_3)_2$.[9] This suggested the $Pt(PEt_3)_2$ fragment could be generated in situ photochemically from $Pt(PEt_3)_2(C_2O_4)$, 1, and its reactions studied *under mild conditions*. Because triethylphosphine is both sterically undemanding and electron-rich, $Pt(PEt_3)_2$ should be highly reactive.[10] Furthermore, this photochemical procedure could provide a convenient route to platinum(0) and platinum(II) complexes containing two triethylphosphine ligands; the only side product of the synthesis would be carbon dioxide.

Complex 1 can be prepared[11] from *cis*-$Pt(PEt_3)_2Cl_2$ and $K_2C_2O_4{\cdot}H_2O$ as white crystals, soluble in polar solvents; it is air-stable and unreactive in the absence of UV light, both as a solid and in solution, but it is photochemically reactive. The $^{31}P\{^1H\}$ NMR and IR spectra of 1 are consistent[12] with the square planar geometry shown in Scheme I. Several experimental facts support the hypothesis that UV irradiation of 1 generates $Pt(PEt_3)_2$. Irradiation of solutions of 1 in the presence of donor and acceptor ligands, L, leads to formation of zerovalent complexes $Pt(PEt_3)_2L_n$ (Scheme I). If 1 is irradiated in the presence of substrates XY that can undergo oxidative addition, platinum(II) complexes $Pt(PEt_3)_2XY$ form.[13] Two

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(2) Otsuka, S.; Yoshida, T.; Matsumoto, M.; Nakatsu, K. *J. Am. Chem. Soc.* 1976, *98*, 5850–5857.

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(4) Abbreviations: Me = methyl; Et = ethyl; Ph = phenyl; *i*-Pr = isopropyl; c-Hx = cyclohexyl; *t*-Bu = *tert*-butyl.

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(8) The species $Pt(PEt_3)_2$ is not seen spectroscopically, e.g., by ^{31}P NMR spectroscopy. Kinetically significant quantities of $Pt(PEt_3)_2$ could, however, be present in solutions of $Pt(PEt_3)_3$. For example, the results of variable-temperature NMR line-shape analysis suggest that $Pt(PEt_3)_3$ exchanges with free PEt_3 by both associative and dissociative pathways.[7]

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(10) Trialkylphosphines are known to greatly increase the nucleophilic reactivity of platinum(0) complexes compared with that of triarylphosphine analogues; see ref 5.

(11) Metathesis of *cis*-$Pt(PEt_3)_2Cl_2$ (Parshall, G. W. *Inorg. Synth.* 1970, *12*, 26–33) with $K_2C_2O_4{\cdot}H_2O$ in equal volumes of hot methanol and water, followed by reduction of the liquid volume and cooling, produces off-white crystals of 1. Recrystallization from dichloromethane/diethyl ether produces pure white crystals of 1 in 85% yield. Anal. Calcd: C, 32.37; H, 5.82; P, 11.93; Pt, 37.56. Found: C, 32.38; H, 5.76; P, 11.98; Pt, 37.80. Ir (CH_2Cl_2): 1704 (vs), 1681 (s), 1670 (m), 1458 (w), 1366 (s), 1042 (sh), 1036 (m), 792 (m) cm^{-1}. UV-Vis (CH_3CN): λ_{max}, nm (ϵ, M^{-1} cm^{-1}) 206 (2.3 × 10^4), 236 (8.3 × 10^3), 258 (3.1 × 10^3), 286 (7.5 × 10^2).

(12) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd Ed.; Wiley: New York, 1978; pp 233–236.

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