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CHEMISTRY OF HETEROCYCLIC COMPOUNDS

LV *. PLATINUM(0) COMPLEXES OF HETEROCYCLIC ACETYLENES: BIS-LITHIATION

GEORGE R. NEWKOME * and MASAYOSHI ONISHI **

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803 (U.S.A.)

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Summary

Low temperature bis-metal—halogen exchange on a platinacyclic moiety is reported to occur without cleavage of the zero-valent platinum—alkyne bond(s). The metallation procedure affords a convenient, mild route to metalate, dehalogenate, label, and/or functionalize metallacycles.

Introduction

The potential utility of transition metal—alkyne complexes as reagents in organic synthesis has attracted considerable attention [3,4]. However, skeletal, structural modification of such complexes has been limited by the lability of the strained metal—carbon bond(s). Zero-valent platinum—alkyne complexes have been shown to easily rupture the platinacyclic ring to afford σ-vinylplatinum(II) derivatives upon treatment with dilute mineral acids [5,6] or to dissociate the initial alkyne upon action of olefins [6], chloroform [7], alcoholic mercuric chloride [2], or another acetylene [1,2,8]. Although V undergoes ligand—ligand exchange and complexation to generate stable bicyclic systems [2], no successful ligand metallations, remote from the carbon—platinum bond, have been reported on such complexes without decomposition of the metallacyclic ring. We herein report the first successful bis-metal—halogen exchange on bis(triphenylphosphine)[bis(6-bromo-2-pyridyl)acetylene]platinum, which affords a convenient, mild procedure to metallate and functionalize these metallacycles without cleavage of the transition metal—carbon bond.

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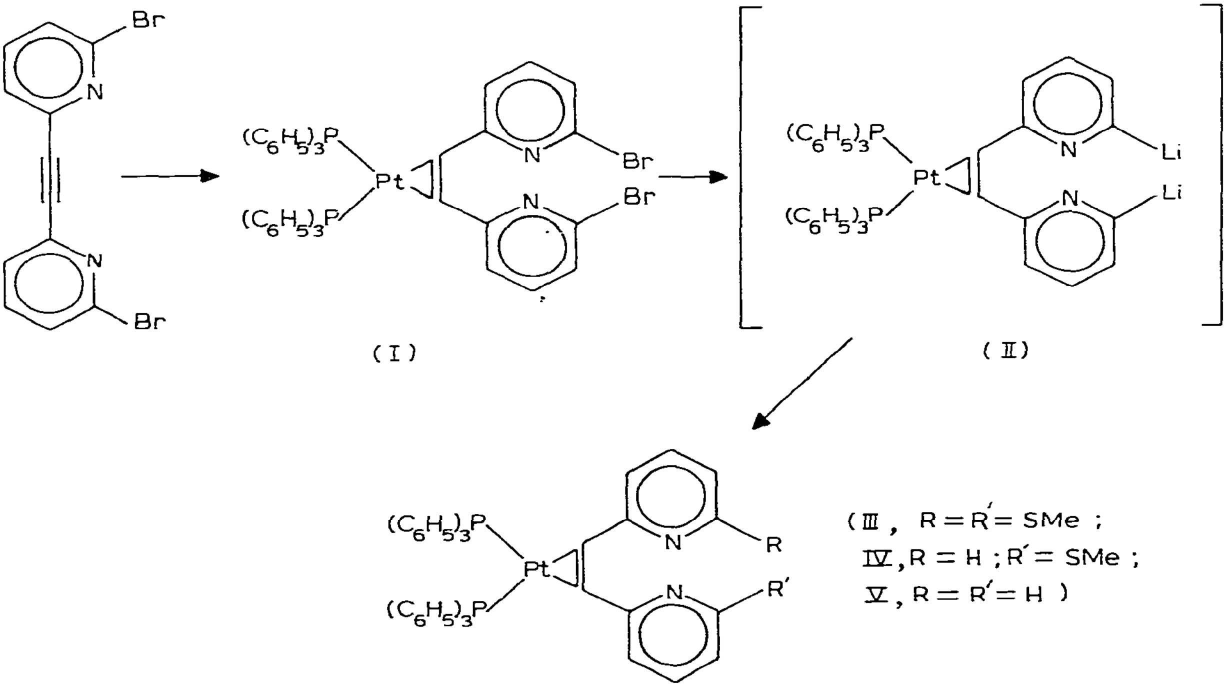
* Previous related parts in this series see ref. 1 and 2.

** On leave from Nagasaki University, Nagasaki, Japan (1979—1980).

Results and discussion

We recently reported the successful synthesis of 2,6-dilithiopyridine by metal—halogen exchange [9]. Application of low temperature metal—halogen exchange procedures, devised by Parham and coworkers [10], to electron-poor heterocyclic systems has now been demonstrated and the selectivity and mildness of the exchange process has been uniquely probed with platinacycle I. Treatment of $[(C_6H_5)_3P]_2Pt^0$, generated from *cis*-$[(C_6H_5)_3P]_2Cl_2Pt^{II}$ and hydrazine hydrate [11], with bis(6-bromo-2-pyridyl)acetylene [12,13] * gave the desired platinacycle I in 25% yield and a 3/2-acetyleneplatinum complex, $\{(acetylene)_3Pt_2[(C_6H_5)_3P]_4\}$ was isolated, and upon attempted thick-layer chromatography, the latter was transformed to the desired I. Similar 2/1 and 2/2 complexes have been reported recently by Stone et al. [15].

When a tetrahydrofuran solution of I, cooled to $\lesssim -90^\circ$C under an argon atmosphere, was treated with two equivalents of n-butyllithium, the initial yellow solution turned reddish-brown within minutes. After 4 h, the lithiated complex II was treated with dimethyl disulfide at $< -80^\circ$C. The resulting product was chromatographed and recrystallized to give (21%) III as yellow microcrystals. The upfield position of the *S*-methyl singlet (δ 2.06 ppm) is indicative of retention of the platinacyclic moiety. A minor product was isolated (2.3%) and shown to be IV, which resulted from the presence of traces of moisture in competition with trapping of II with dimethyl disulfide.



(I)

(II)

(III, R = R' = SMe ;
IV, R = H ; R' = SMe ;
V, R = R' = H)

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* Pyridylacetylenes were conveniently prepared (50—80%) by the reaction of halopyridines and acetylenes in the presence of a palladium catalyst and triethylamine solvent [13,14].

When the bis-lithioplatinacycle II was quenched with anhydrous methanol at —90°C, V was isolated (32%) and shown to be identical in all respects to a known sample. Under these metal—halogen exchange conditions, no products arising from monometallation were detected; however, with decreased quantities of metallating reagents such products would be anticipated.

Treatment of pyridylacetylenes with strong nucleophiles, e.g., RLi, affords predominantly products resulting from Michael-type addition to the acetylene bond [12,16]; thus, I can now be functionalized, then transformed back to the free functionalized dipyridylacetylene by treatment of desired platinacycle with alcoholic mercuric chloride.

Halogen—metal exchange at low ($\lesssim$ —90° C) temperatures has been demonstrated to be very selective even in the presence of internal electrophilic sites [10]. The temperature range is, however, critical, since at higher temperatures ($\gtrsim$ —80° C) competitive reactions in these organometallic systems begin to occur. Solvent effects are also important in these systems and THF has been demonstrated to be superior to diethyl ether [9].

This successful extension of low temperature metal—halogen exchange to functionalize strained transition metal complexes suggests further application to other organometallic systems; further studies are in progress.

Experimental

All melting points were taken in evacuated capillary tubes with a Thomas—Hoover Uni-Melt melting point apparatus and are uncorrected. NMR spectra were obtained in $CDCl_3$ solutions with Me_4Si, as the internal standard (δ = 0 ppm) and recorded on either a Varian Associates A-60A or Bruker WP-200 NMR. For preparative ThLC, 2 mm Brinkman silica gel P/UV-254-366 or aluminium oxide (Type T) HF-254-366 plates were used, eluting with the stipulated solvent system. The recorded R_f values were determined by a standardized thin-layer chromatography plates (0.025 mm) with the stated solvents. Mass spectra (MS) were obtained on a Hewlett Packard Model 5986 GC/MS system with direct inlet attachment. Infrared (IR) spectra were recorded on a Perkin—Elmer 621 spectrometer. Elemental analyses were performed by Mr. R. Seab in these laboratories.

Tetrahydrofuran (THF) was dried and distilled under nitrogen from lithium aluminum hydride before use. All solvents were dried and distilled by standard procedures. All reactions were conducted under an argon atmosphere.

Preparation of bis(triphenylphosphine)[bis(6-bromo-2-pyridyl)acetylene]-platinum. A suspension of *cis*-dichlorobis(triphenylphosphine)platinum (1.25 g, 1.58 mmol) in absolute ethanol (30 ml) was treated with a solution of hydrazine hydrate (4 ml) in ethanol (5 ml) at 45°C [11]. After the mixture was stirred for 30 minutes, bis(6-bromo-2-pyridyl)acetylene (m.p. 212—213°C (dec), 1.05 g, 3.1 mmol) [12,13] was added, then stirred for 12 h at ca. 45°C. The solvent was concentrated in vacuo to afford a residue which was extracted with benzene. The solid was triturated with boiling ethanol and filtered. Removal of the solvent afforded a solid, which was chromatographed (TLC), eluting with cyclohexane/ethyl acetate (2/1) to give (25%) the platinacycle I, as pale yellow microcrystals: m.p. 205—206°C (dec, ethanol); 420 mg (0.4 mmol); R_f 0.76; IR

(KBr) 1748 (C≡C), 1568 (Pyr), 1538, 1428 cm^{-1}; MS (70 eV) *m/e* 340 (30.3, $C_{12}H_6N_2Br_2$), 338 (49.7), 336 (30.2), 262 [100, $C_{18}H_{15}P$]. 259 (44.1, $C_{12}H_6N_2Br$), 257 (42.2).

Anal. Found: C, 54.54; H, 3.47; N, 2.65. $C_{48}H_{36}N_2Br_2P_2Pt$ calcd.: C, 54.51; H, 3.43; N, 2.65%.

Dilithiation of the dibromoplatinacycle (I). A quenching with dimethyl disulfide. To a THF solution of I (138 mg, 0.13 mmol) cooled to −90° C (petroleum ether/liquid nitrogen) under an argon atmosphere, n-butyllithium (0.31 mmol) in hexane was added. The initial yellow coloration immediately changed to reddish brown. The mixture was stirred while maintaining the temperature at −88°C to −92°C for 4 h. Dimethyl disulfide (40 mg, 0.43 mmol) in THF was added; the color changed into orange yellow. After stirring for 2 additional hours and addition of methanol (3 ml) at ca. −80°C, the mixture was warmed to 25°C, and filtered. The filtrate was evaporated to dryness in vacuo (without heating). The resulting solid was chromatographed (TLC) on silica gel, eluting with cyclohexane/ethyl acetate (3/1); then the desired bands were extracted with a mixture of ethanol/diethyl ether (1/3). The first fraction was recrystallized from CH_2Cl_2/hexane to give III, as yellow microcrystals: m.p. 179—182°(dec); 26 mg (21%) R_f0.67; IR (KBr) 1749 (C≡C), 1567 (Pyr), 1550, 1437 cm^{-1}; NMR ($CDCl_3$) δ 2.06 ppm (s, S—Me, 6 H); MS (70 eV) *m/e* 272 (38.9, $C_{14}H_{12}S_2N_2$), 262 (100, $C_{18}H_{15}P$). Anal. Found: C, 60.74; H, 4.04; N, 2.86. $C_{50}H_{42}N_2P_2S_2Pt$ calcd.: C, 60.54; H, 4.27; N, 2.82%.

A minor product was isolated and recrystallized from CH_2Cl_2/hexane to give IV: m.p. 194—196° C (dec); 3 mg (2.3%); R_f 0.45; NMR ($CDCl_3$) δ 2.09 (s, S—Me, 3 H), 8.34 ppm (bd, 6-pyr-H, *J* 4.8 Hz, 1 H); MS (70 eV) *m/e* 262 (56.2, $C_{18}H_{15}P$), 226 (52.8, $C_{13}H_{10}SN_2$), 183 (100, $C_{12}H_8P$).

B. Quenching with methanol. The initial generation of II was carried out as described above, except then complex II was treated with methanol. After stirring at −90° C for 2 h and standard workup, the resulting solid was chromatographed (TLC) on alumina eluting with cyclohexane/ethyl acetate (2/1), and then recrystallized from diethyl ether/petroleum ether to give V as yellow microcrystals: m.p. 186—189°C (dec); 32%; R_f 0.51; IR (KBr) 1750 (C≡C), 1581 (Pyr), 1561, 1463, 1427 cm^{-1}; NMR ($CDCl_3$) δ 8.30 ppm (bd, 6-pyr H, *J* 4.8 Hz); MS (70 eV) *m/e* 262 (100, $C_{18}H_{15}P$), 180 (80.7, $C_{12}H_8N_2$). Anal. Found: C, 64.38; H, 4.60; N, 2.83. $C_{48}H_{38}N_2P_2Pt$ calcd.: C, 64.07; H, 4.26; N, 3.11%.

Regeneration of di(2-pyridyl)acetylene from bis(triphenylphosphine)[di-(2-pyridyl)acetylene]platinum. An ethanolic solution of V (90 mg) was refluxed under nitrogen, then one equivalent of mercuric chloride in ethanol was added. After 30 minutes, the mixture was cooled and filtered to remove $PtCl_2[P(C_6H_5)_3]_2$ and metallic mercury. The filtrate was concentrated and chromatographed (TLC) eluting with ethyl acetate cyclohexane (1/1) to give (94%) di-2-pyridylacetylene: m.p. 69—71°C.

Under similar conditions, platinacycle I was decomposed to give (83%) of the starting bis(6-bromo-2-pyridyl)acetylene: m.p. 212—213° C.

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