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Notes

Two Alternative, Convenient Routes to Bis(diphenylacetylene)platinum(0)

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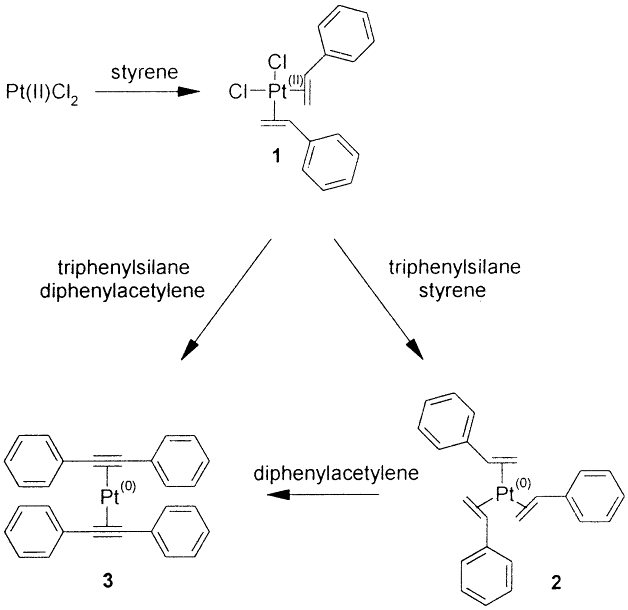
Summary: Two new synthetic routes are presented that allow the convenient preparation and isolation of bis(diphenylacetylene)platinum(0) under ambient conditions. The first procedure is based on a ligand exchange reaction between $Ph{-}C{\equiv}C{-}Ph$ *and tris(styrene)platinum(0). The second framework relies on the reduction of cis-*$[PtCl_2(PhCH{=}CH_2)_2]$ *with triphenylsilane in the presence of diphenylacetylene.*

Zerovalent platinum complexes are important for a wide variety of homogeneous catalytic processes.[1] Bis(η^2-alkyne)platinum(0) complexes represent a particularly interesting subgroup that is viewed as a family of (potentially) useful synthetic intermediates, since the alkyne ligands are readily replaced by other donor ligands such as PMe_3, PEt_3, PPh_3, and *t*-BuCN.[2−4] These alkyne complexes are frequently synthesized by ligand exchange reactions from bis(1,5-cyclooctadiene)platinum(0)[2,3] or tris(η^2-ethylene)platinum(0).[4] However, the synthesis of the latter compounds is laborious and requires rigorous exclusion of oxygen and water.[5,6] The preparation of bis(η^2-alkyne)platinum(0) complexes via decomposition of bis(4-penten-1-yl)platinum(II) in the presence of alkynes has also been reported,[7] but the related procedures require not only a protective atmosphere but also high pressure, which renders the preparation intricate. Another method starts from the hydrosilylation catalyst hexachloroplatinic(IV) acid, which is heated in the presence of an excess of *sym*-tetramethyldivinylsiloxane and exposed in situ to alkynes.[8] Surprisingly, $H_2[PtCl_6]\cdot xH_2O$ is reduced without explicite addition of a reducing agent. Thus, the reduction appears to be induced by impurities, subjecting this reaction to some imponderables. Indeed, it is well established that the reduction of hexachloroplatinic(IV) acid in hydrosilylation catalysis is accompanied by an induction period of variable length.[9]

Scheme 1. Synthesis of $[Pt(\eta^2\text{-}Ph{-}C{\equiv}C{-}Ph)_2]$ **(3) through (i) Ligand Exchange between** $[Pt(PhCH{=}CH_2)_3]$ **(2) and** $Ph{-}C{\equiv}C{-}Ph$**, and (ii) Reduction of *cis*-**$[PtCl_2(PhCH{=}CH_2)_2]$ **(1) with Triphenylsilane in Presence of** $Ph{-}C{\equiv}C{-}Ph$



Here, we describe two simple, well-defined and reproducible methods for the synthesis of $[Pt(\eta^2\text{-}Ph{-}C{\equiv}C{-}Ph)_2]$[2,8] (**3**), which can be performed under ambient conditions. The first procedure is based on a ligand exchange reaction between $Ph{-}C{\equiv}C{-}Ph$ and tris(styrene)platinum(0) (**2**). The latter complex is readily obtained by reduction of *cis*-$[PtCl_2(PhCH{=}CH_2)_2]$[10] (**1**) with triphenylsilane *in a styrene solution.*[11] The styrene solution of **2** is stable for months even in the absence of a protective gas. Extensive NMR investigations revealed

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that **2** readily converts in situ into a variety of Pt(0) derivatives by ligand exchange, in particular with 1,2-bis(diphenylphosphino)ethane (diphos), P(OEt)$_3$, and 1,5-cyclooctadiene (cod).[11] Regrettably, however, neither **2** nor derivatives prepared via the latter could be *isolated* in the past from the styrene solution. We now have found that treating a styrene solution of **2** with Ph$-$C$\equiv$C$-$Ph leads to the formation of [Pt(η^2-Ph$-$C$\equiv$C$-$Ph)$_2$] (**3**) (Scheme 1). In situ ^{195}Pt NMR experiments revealed that the signals related to **2** at $-$5874.8 and $-$5893.2 ppm are fully suppressed upon addition of 2 equiv of Ph$-$C$\equiv$C$-$Ph per Pt atom, and the only detectable resonance is that of **3** at $-$3548 ppm. Thus, even in the presence of a large excess of styrene, the styrene ligands coordinated to Pt(0) are very efficiently replaced by Ph$-$C$\equiv$C$-$Ph. In contrast to the in-situ-prepared complexes mentioned above, we were able to isolate **3** by precipitation upon addition of pentane.[12,13] We subsequently explored the possibility of preparing **3** directly through the reduction of *cis*-[PtCl$_2$(PhCH$=$CH$_2$)$_2$] with triphenylsilane in the presence of Ph$-$C$\equiv$C$-$Ph (Scheme 1) and under ambient conditions. Gratifyingly, **3** could indeed be isolated with this method in high purity.[14] Preliminary experiments have shown that also [Pt(η^2-HOMe$_2$C$-$C$\equiv$C$-$CMe$_2$OH)$_2$] can be synthesized by this framework, while attempts to prepare [Pt(cod)$_2$] using the same procedure have hitherto been unsuccessful.

Thus, in summary, we have demonstrated two new and convenient routes for the synthesis of bis(η^2-alkyne)platinum(0). Both methods depart from readily accessible, chemically stable intermediates, are based on straightforward and undemanding reaction conditions, and afford the desired product in high purity.

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[12] Ph$-$C$\equiv$C$-$Ph (3.00 g, 16.9 mmol) was added to a solution of Pt(PhCH$=$CH$_2$)$_3$ ($\sim$0.37 mmol) in styrene (20 mL), and styrene was distilled off (10 mbar, 50 °C) to reduce the volume of the mixture to 5 mL. Pentane (15 mL) was added, and the mixture was cooled to 0 °C. The resulting solid was filtered off, washed with pentane, dried in vacuo, and reprecipitated from CH$_2$Cl$_2$/pentane (5/30 mL) at $-$78 °C to afford a pale yellow solid (117 mg, $\sim$57%). ^{195}Pt NMR (64 MHz, CD$_2$Cl$_2$, 263 K): δ $-$3553 ppm. Anal. Calcd for C$_{28}$H$_{20}$Pt: C, 60.98; H, 3.65. Found: C, 60.81; H, 4.06.

[13] Note that the reactions reported here have not yet been optimized for yield.

[14] Triphenylsilane (439 mg, 1.68 mmol) was added to a mixture of [PtCl$_2$(PhCH$=$CH$_2$)$_2$] (400 mg, 0.844 mmol) and Ph$-$C$\equiv$C$-$Ph (1.50 g, 8.46 mmol) in CH$_2$Cl$_2$ (16 mL), and the reaction mixture was stirred for 30 min. Aqueous ammonia (37 mL, 3%) was added, and the mixture was vigorously stirred for 90 min. The organic phase was separated off, extracted with water (33 mL), and filtered through a 3 cm plug of Alox (basic, activity I), which was subsequently rinsed with CH$_2$Cl$_2$ (16 mL), and the organic layers were combined. CH$_2$Cl$_2$ was distilled off to reduce the volume of the mixture to 5 mL, pentane (20 mL) was added, and the mixture was cooled to 0 °C. The resulting solid was filtered off, washed with pentane, and dried in vacuo to afford a pale yellow solid (121 mg, 26%). ^{195}Pt NMR (64 MHz, CD$_2$Cl$_2$, 263 K): δ $-$3553 ppm. Anal. Calcd for C$_{28}$H$_{20}$Pt: C, 60.98; H, 3.65. Found: C, 61.14; H, 4.13.