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Expedient, Direct Synthesis of (L)Pt(0)(1,6-diene) Complexes from H_2PtCl_6

Guillaume Berthon-Gelloz,[†] Jean-Marc Schumers,[†] Fabio Lucaccioni,[†] Bernard Tinant,[†]
Johan Wouters,[‡] and István E. Markó*,[†]

*Département de Chimie, Université catholique de Louvain, Place Louis Pasteur 1,
1348 Louvain-la-Neuve, Belgium, and Département de Chimie, Facultés Universitaires Notre-Dame de la
Paix, Rue de Bruxelles 61, 5000 Namur, Belgium*

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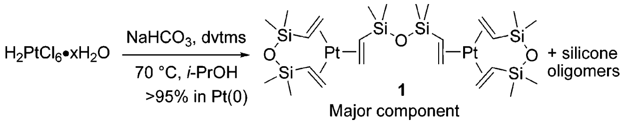
*Summary: The one-pot synthesis of useful [$Pt_2(0)(\eta^4$-1,6-diene$)_3$] complexes, directly from $H_2PtCl_6\cdot xH_2O$, has remained an unaddressed problem. We have found that the treatment of an i-PrOH solution of $H_2PtCl_6\cdot xH_2O$ by $(Me_3SiO)_2MeSi(CH{=}CH_2)$, in the presence of allyl ether (AE), followed by reaction of the in situ generated Pt(0) species with IPr carbene (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) enables the isolation of (IPr)Pt(AE) (**1**) in 50−70% yield. The scope of this method has been extended to other (L)Pt(1,6-diene) complexes (L = 1,3-dicyclohexylimidazol-2-ylidene, triphenylphoshine; 1,6-diene = diethyl 2,2-diallylmalonate (DAM)), and the molecular structure of the (IPr)Pt(DAM) (**4**) complex has been unequivocally determined by a single-crystal X-ray diffraction analysis. These results are significant for the formation of active L−Pt-(0) fragments in catalysis.*

Introduction

Platinum(0) complexes play a prominent role in homogeneous catalysis. They are also useful starting materials for the synthesis of various organometallic species.[1] Organoplatinum derivatives bearing alkene ligands have been found to be uniquely active catalysts for the hydrosilylation of olefins and alkynes.[2] The most notable homoleptic Pt(0)(alkene)$_3$ complex is Karstedt's catalyst (Scheme 1, **1**)[3] which is one of the most widely used organometallic reagents for the hydrosilylation reaction. It is routinely prepared on the kilogram scale, in high yield and in a single step, from H_2PtCl_6 (Scheme 1).[2,4,5]

The straightforward access to Karstedt's catalyst has made it the source of choice for the synthesis of a plethora of (L)Pt-(0)(dvtms) complexes (L = ligand, dvtms = divinyltetramethyldisiloxane).[3,6−13] However, one particularly limiting factor in this methodology is that the diene fragment cannot be varied at will and the dvtms ligand can be displaced only by electron-poor alkynes, such as dimethylacetylenedicarboxylate.[14] This unexpected inertia is due to the strongly coordinating nature of the dvtms ligand to the Pt(0) center. The thermodynamic stability of (L)M(0)(η^4-1,6-diene) complexes has been established in a study by Pörschke et al. and is depicted in Figure 1.[15] Consequently, (L)Pt(0)(η^4-1,6-diene) complexes cannot be accessed by the simple displacement of the dvtms moiety in (L)-Pt(0)(η^4-dvtms) derivatives by another diene.

Scheme 1. Formation of Karstedt's Catalyst (dvtms = divinyltetramethyldisiloxane)



Results from Osborn, Elsevier, and our group have shown that the nature of the alkene fragment is a key parameter in determining the stability and the hydrosilylating activity of (L)-Pt(0)(η^2-alkene)$_2$ and (L)$_2$Pt(0)(η^2-alkene) complexes, the rate-limiting step of the catalyst activation being the decoordination of one of the alkene moieties.[11,13,16−19] The influence of so-called "spectator" dienes (e.g., *cis*,*cis*-1,5-cyclooctadiene (cod), *trans*,*trans*-dibenzylidene acetone (dba), 2,5-bicyclo[2.2.1]-heptadiene) on the overall catalytic activity of precatalysts bearing these ligands has recently become widely recognized.[20] For example, the influence of spectator dba diene has been elegantly demonstrated by Fairlamb et al. for cross-coupling reactions catalyzed by Pd-dba-type complexes.[21,22] In these studies, the electronic nature of the substituents on the aromatic rings of dba was shown to have significantly altered the overall

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* To whom correspondence should be addressed. E-mail: marko@chim.ucl.ac.be. Phone: +32/10478773. Fax: +32 10472788.

[†] Université catholique de Louvain.

[‡] Facultés Universitaires Notre-Dame de la Paix.

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(5) Although **1** is the major component of Karstedt's catalyst, the reaction product from the synthesis is a complex and dynamic mixture of different Pt(0) species, which must be stored with several equivalents of the divinyltetramethyldisiloxane (dvtms) ligand to ensure long-term stability.

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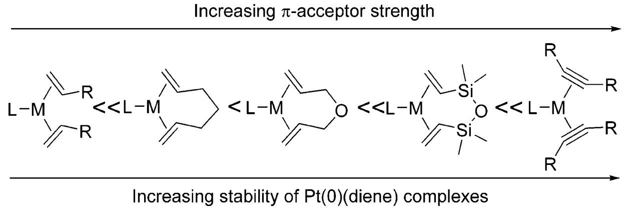


Figure 1. Sequence of increasing acceptor strength of alkenes, 1,6-dienes, and alkynes and of increasing stability of the corresponding (L)M(η^4-1,6-diene), (L)M(η^4-alkene)$_2$, and (L)M(η^4-alkyne)$_2$ complexes.

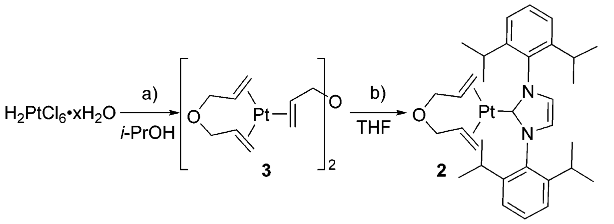
catalytic activity and this, even in the presence of other ancillary ligands on palladium.

Existing syntheses of (L)Pt(0)(alkene)$_2$ derivatives employ either Pt(0)(cod)$_2$ or Pt(0)(nbn)$_3$ (nbn = bicyclo[2.2.1]hept-2-ene) as starting materials. The latter complexes are prepared by the reduction of PtCl$_2$(cod) by Li$_2$(cot) (cot = cyclooctatetraene), in the presence of a large excess of alkene (e.g., nbn), to yield the homoleptic Pt(η^2-alkene)$_3$ complexes.[23] Such an approach not only is fastidious but also requires the rigorous exclusion of oxygen and water. A report by Ogoshi and Kurosawa describes the use of SmI$_2$ instead of Li$_2$(cot) as the reducing agent. Again, this method employs an expensive and sensitive reducing agent.[24] Pregosin and Caseri described an interesting process based upon the reduction of PtCl$_2$(CH$_2$=CHPh)$_2$ by Ph$_3$SiH, in the presence of excess styrene, to afford the extremely sensitive Pt(0)(CH$_2$=CHPh)$_3$ complex. However, the scope of this method remains to be delineated.[25,26] Another reduction protocol relies upon the electron-transfer reaction between a Ni(0) derivative ([Ni(bpy)(cod)] (bpy = 2,20-bipyridine)) and a Pt(II) complex, to yield the corresponding Pt(0) species.[27] Unfortunately, this approach requires the use of Ni(cod)$_2$, which is difficult to handle.

At this stage, and to the best of our knowledge, no efforts have been made to expand the scope of the reduction process involved in the formation of Karstedt's catalyst to dienes other than divinylsilanes. Detailed studies by Lewis and Lappert on the mode of formation of Karstedt's catalyst **1** have shown that the dvtms diene acts not only as a stabilizing ligand for Pt(0) but also as a reducing agent for Pt(IV) or Pt(II) species to Pt(0).[3,28,29] It should therefore be possible to use a poorly coordinating vinylsilane, in the presence of a diene, to effect the reduction of H$_2$PtCl$_6$ to Karstedt-type complexes.

Herein, we wish to report a practical and widely applicable two-step sequence for the synthesis of a family of (L)Pt(0)(η^4-1,6-diene) complexes starting from H$_2$PtCl$_6$. In these organometallic derivatives, L can be a donor ligand such as a phosphine or an N-heterocyclic carbene (NHC). The key to our successful approach is the use of a monomeric and hydrolytically stable vinylsiloxane, instead of dvtms, as a mild reducing agent. This synthesis has several significant advantages: it does not require glovebox or Schlenck techniques, employs readily available starting material, and can be carried out on a relatively large scale (20 mmol).

Table 1. Optimization of the Two-Step Reaction Sequence for the Synthesis of (IPr)Pt(η^4-AE) (2)[a]



entry	reducing agent (equiv)	AE (equiv)	t (h)	IPr•HCl/t-BuOK (1:1, equiv)	yield (%)[b]
1[c]	Et$_3$SiVi (5)	5	10		*c*
2	(EtO)Me$_2$SiVi (5)	5	2		60[d]
3[e]	(Me$_3$SiO)Me$_2$SiVi (5)	5	2		*f*
4	(Me$_3$SiO)Me$_2$SiVi (2.5)	10	6	1.1	18
5	(Me$_3$SiO)$_3$SiVi (5)	10	6	1.1	40
6	(Me$_3$SiO)$_2$MeSiVi (5)	12	10	1.2	47
7	(Me$_3$SiO)$_2$MeSiVi (5)	10[g]	10	1.1	43
8	**(Me$_3$SiO)$_2$MeSiVi (5)**	**12**	**48**	**1.6**	**70**
9[h]	(Me$_3$SiO)$_2$MeSiVi (5)	10	7	1.1	*i*
10	(Me$_3$SiO)$_2$MeSiVi (5) + KF[j]	10	15	1.1	

[a] Reaction conditions: (1) H$_2$PtCl$_6$•xH$_2$O (40% Pt; 150 mg, 0.30 mmol), *i*-PrOH (0.3 M), 0.5 h, 60 °C; NaHCO$_3$ (200 mg, 8 equiv), 10 min; reducing agent, AE, 60 °C; (2) THF (0.15 M), IPr•HCl; *t*-BuOK, Ar, 16 h. [b]Isolated yield after column chromatography. [c]No reaction. [d]Only (IPr)Pt(dvtms) was isolated. [e]Reaction temperature = 75 °C. [f]Formation of platinum black.[g]AE added prior to reducing agent addition. [h]H$_2$PtCl$_6$•xH$_2$O, AE, vinylsilane, 60 °C, 4 h; NaHCO$_3$. [i]Complex reaction mixture. [j]KF (6.5 equiv). AE = diallyl ether, Vi = vinyl.

Results and Discusion

The direct characterization of Karstedt-type complexes (Pt$_2$-(1,6-diene)$_3$) is difficult due to their dynamic properties in solution and to the unstable nature of the isolated Pt$_2$(1,6-diene)$_3$ species (without excess diene). It is operationally simpler to react the Pt(0)$_2$(1,6-diene)$_3$ solution with a coordinating ligand and to isolate the more stable, mononuclear (L)Pt(1,6-diene) complex, to evaluate the efficiency of the reduction process. Therefore, we focused our efforts on the synthesis of the (IPr)-Pt(η^4-AE) (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), AE = allyl ether) derivative (**2**), which displayed interesting catalytic activities in the hydrosilylation of alkynes and which was required in substantial amounts. The intermediate complex Pt$_2$(AE)$_3$ (**3**) has been previously fully characterized by Pörschke and co-workers.[15,30]

At the onset of our study, we adapted conditions from the synthesis of Karstedt's catalyst by replacing the dvtms ligand by allyl ether and by employing triethylvinylsilane as the reducing agent (Table 1, entry 1). After prolonged heating at 60 °C, no formation of Pt(0) was observed, as judged by the absence of nonpolar UV-active Pt(0) species on the TLC plate.[31] Hiyama and Denmark have demonstrated the necessity for the silicon center to bear at least one heteroatom for successful transmetalation to occur in palladium-catalyzed cross-coupling reactions of organosilicon compounds.[32] In analogy, we used (EtO)Me$_2$SiVi (Vi = vinyl) as a reducing agent (Table 1, entry 2) and were gratified to observe the smooth formation of Pt(0) species. However, even under these mild conditions, (EtO)Me$_2$SiVi redistributed to form the (Me$_2$ViSi)$_2$O (dvtms) diene.[13] This

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(31) Pt(0)−alkene complexes display very strong absorption in their UV spectra. Karstedt's catalyst is an apolar complex, R_f(Hex) = 0.6.

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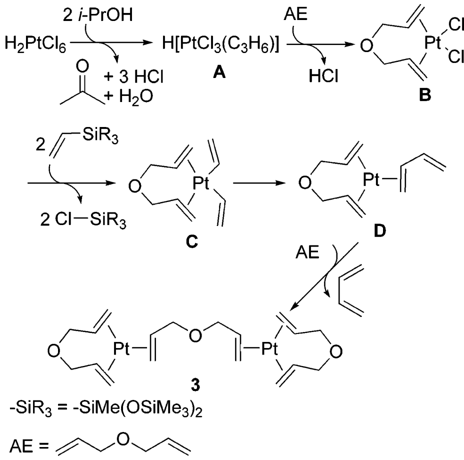
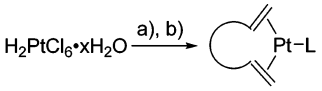
Scheme 2. Proposed Mechanism for the Main Reduction Pathway of H_2PtCl_6 into the Pt(0) Complex 3

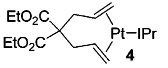
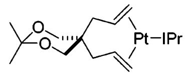
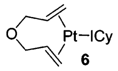
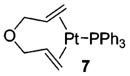


reorganization of the vinylsilane led to the isolation of the (IPr)-Pt(η^4-dvtms) complex, which is more stable than the corresponding (IPr)Pt(η^4-AE) derivative. The driving force behind the formation of dvtms diene from (EtO)Me_2SiVi is the highly stable Si−O−Si linkage. To overcome this issue, we opted for the use of (Me_3SiO)Me_2SiVi, which already contains the Si−O−Si motif. Although, initial trials at 75 °C were unsuccessful (Table 1, entry 3), due to decomposition of the Pt(0) species formed, lowering the reaction temperature to 60 °C and using 10 equiv of AE led to the isolation of the desired complex in a modest but encouraging 18% yield (Table 1, entry 4). Next, we examined the influence of increasing amounts of vinylsilane (5 equiv) and varied the number of heteroatoms present on the silicon atom (Table 1, entries 5 and 6). Both changes had a positive effect, resulting in a 47% isolated yield of **2** (Table 1, entry 6), although the electronic influence on the silicon center proved to be moderate. The $(Me_3SiO)_2MeSiVi$ vinylsilane was preferred over (Me_3SiO)Me_2SiVi and $(Me_3SiO)_3SiVi$ because it is more readily available. Adding the allyl ether to form the $PtCl_2$(η^4-AE) complex prior to the reducing agent had no significant effect on the yield (Table 1, entry 7). Gratifyingly, by performing the reduction during 48 h and by generating 1.6 equiv of the IPr carbene in the second step, the desired complex could be isolated in 70% yield over the two steps (Table 1, entry 8). A control experiment (Table 1, entry 9) was conducted in which $(Me_3SiO)_2MeSiVi$ and AE were reacted for 4 h at 60 °C before addition of the sodium bicarbonate. This led to a complex reaction mixture that contained none of the desired complex **2**. The highly acidic nature of H_2PtCl_6 is presumably responsible for the redistribution of the vinyl silane and the isomerization and subsequent hydrolysis of the allyl ether.[28] We sought to further improve the transmetalation process by adding a fluoride source (Table 1, entry 10). This led to the observation of scores of Pt(0) species (TLC analysis). After reaction with the IPr carbene, an intractable mixture of complexes was obtained probably due to a fluoride-catalyzed redistribution of $(Me_3SiO)_2MeSiVi$ into silicone oligomers.

Although the exact nature of the $Pt(0)_2(AE)_3$ (**3**) formed was difficult to elucidate by ^{1}H and ^{13}C NMR, due to the fluxional nature of such complexes, the ^{195}Pt NMR displayed only one Pt signal with a chemical shift of −6365 ppm. This shift is perfectly in line with the ^{195}Pt chemical shift of the analogous Karstedt's catalyst (−6156 ppm). The lower chemical shift of the homoleptic complex $Pt_2(AE)_3$ (**3**) relative to $Pt_2(dvtms)_3$ is indicative of a more electron-rich platinum center due to lesser back-bonding onto the olefins.[3]

Table 2. Synthesis of (L)Pt(1,6-diene) Complexes[a]



Entry	Complex	^{195}Pt shift (ppm)	yield (%)[b]
1	 **4**	-5486	55
2	 **5**	-5453	48
3[c]	 **6**	-5581	40
4[c]	 **7**	-	60

[a] Reaction conditions: (1) $H_2PtCl_6\cdot xH_2O$ (40% Pt), *i*-PrOH (0.2 M), 0.5 h, 60 °C; $NaHCO_3$ (8 equiv), 10 min; $(Me_3SiO)_2MeSiVi$ (5 equiv), 1,6-diene (10 equiv), H_2O (4 equiv), 16 h; filtration (SiO_2), evaporation; (2) THF (0.15 M), ligand (1.5 equiv), 16 h, Ar. [b]Isolated yield after column chromatography. [c]1.0 equiv of ligand added. ICy = 1,3-dicyclohexylimidazol-2-ylidene.

During the scale-up of this reaction on the gram scale, reproducibility issues were unveiled that were eventually traced to the amount of water present in the reaction mixture. Thus, the addition of 4 equiv of water, relative to platinum, enhanced the rate and the amount of Pt(0) complexes formed during the reaction. We believe that the presence of water significantly increases the rate of hydrolysis of the chlorosilane byproduct, formed from the σ-bond metathesis of the Pt−Cl and the Si−Vi linkages (cf. Scheme 2), to yield a stable polysiloxane. Therefore, the formation of the polysiloxane also acts as a thermodynamic driving force for the reaction ($D_{\mathrm{Si-O}} = 136$ kcal mol^{-1} in siloxanes). The use of a mechanical stirrer for larger scale reaction (>5 mmol of Pt), which ensured proper mixing of the heterogeneous reaction media, became mandatory. The sturdiness of this method was probed by carrying out the synthesis on 10 g of H_2PtCl_6; the desired (IPr)Pt(AE) (**2**) complex was obtained in more than 60% overall yield.

A proposed mechanism for this reduction process is outlined in Scheme 2. The first step involves the reduction of H_2PtCl_6 by *i*-PrOH to form the Pt(II) complex **A** (an analogue of Zeise's salt) with concomitant generation of acetone and HCl.[33,34] Organometallic **A** can then undergo a ligand exchange with diallyl ether to produce $PtCl_2$(AE) (**B**). Then, a double transmetalation of the Pt−Cl bonds with the vinyl silane occurs, leading to **C**. The driving force of this process lies in the formation of the Si−Cl bond ($D_{\mathrm{SiCl}} = 117$ kcal mol^{-1} vs $D_{\mathrm{Si-C}} = 90$ kcal mol^{-1}).[35] The resulting chlorosilanes can react further with the isopropyl alcohol or water, in the presence of $NaHCO_3$. Interestingly, this transmetalation appears to occur under neutral conditions ($NaHCO_3$ is added to neutralize the HCl generated so far) and without any specific additives, the only Lewis base present to activate the vinylsilane being the chloride anion. The intermediate **C** can then undergo a reductive elimination to form 1,3-butadiene and the desired Pt(0) species. Evidence for this mechanism is provided by the observation of 1,3-butadiene and

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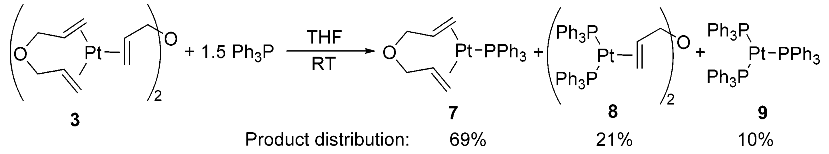
Scheme 3. Product Distribution Observed by ^{31}P NMR with L = Ph_3P



higher order polysiloxanes in earlier studies with dvtms as the reducing agent.[28] The effectiveness of the present method might be partially attributed to the formation of 1,3-butadiene during the reductive elimination of the Pt(II) species to yield Pt(0) derivative **3**. Hence, 1,3-butadiene can act as a transient alkene ligand for Pt(0), preventing the decomposition of this highly reactive species, before being displaced by the more coordinating and stabilizing 1,6-diene.

With a robust method in hand, we set out to synthesize various members of the (L)Pt(1,6-diene) complexes family. The results are depicted in Table 2. The synthesis of Pt(0) derivatives bearing the bulky IPr ligand proceeded smoothly and with reasonable yields (Table 2, entries 1 and 2). However, for complexes **6** and **7**, in which the ICy and Ph_3P ancillary ligands are not sterically hindered, the product distribution becomes more complicated because two or three of these ligands can be easily accommodated around the platinum center and the AE can be readily displaced. This problem is illustrated in Scheme 3. The addition of 1.5 equiv of Ph_3P to the crude $Pt_2(AE)_3$ complex leads to the observation of three types of complexes (determined by ^{31}P NMR), the desired product **7** (69%), along with complexes **8** (21%) and **9** (10%), bearing two and three Ph_3P ligands, respectively. This ligand displacement does not arise with the hindered IPr carbene and is absent if the 1,6-diene ligand is more strongly coordinated to the platinum center (e.g., dvtms). To minimize this problem, exactly 1 equiv (or slightly less) of ligand must be added.

The electronic effect of the modification of the 1,6-diene fragment in the (L)Pt(0) unit can be monitored by ^{195}Pt NMR. We have previously observed that, within a series in which the nature of one of the ligands remains constant, there was a correlation between the thermodynamic stability of a L-Pt(0)-(η^4-1,6-diene) complex and its ^{195}Pt chemical shift.[13] In other words, the higher the chemical shift, the more stable the complex. Thus, the ^{195}Pt NMR chemical shifts of **2** and **4**, which are −5574 and −5486 ppm, respectively, point to a higher stability of **4** over **2**. A slightly lower-field chemical shift, −5453 ppm, is observed for **5**, thereby suggesting that the presence of the cyclic acetonide further reinforces the "Thorpe−Ingold" effect, whereby the *gem*-disubstitution of the two ethyl ester moieties on the diallyl fragment limits their degrees of rotational freedom. We have also correlated the ^{195}Pt shift of a number of complexes with their hydrosilylation activity. These and other observations will be fully detailed in a forthcoming report.

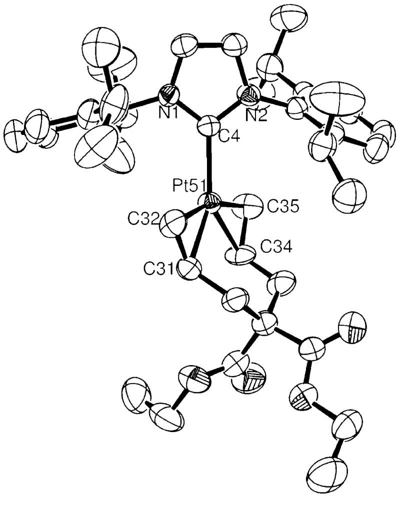


Figure 2. ORTEP plot of (IPr)Pt(DAM) (**4**) with thermal ellipsoids at the 50% probability level. Selected bond distances (Å) and angles (deg): Pt51−C4, 2.067(4); Pt51−C31, 2.122 (4); Pt51−C32, 2.123 (4); Pt51−C34, 2.143 (5); Pt51−C35, 2.144(5); C31−C32, 1.427(8); C34−C35, 1.436(7); C31−C32−C33−C35, −2.2(4); N1−C4−Pt51−C32, −51.2(4).

A crystal of **4**, suitable for X-ray diffraction studies, was grown from a saturated *i*-PrOH solution (Figure 2). The 1,6-heptadiene portion of the diethyl diallylmalonate (DAM) ligand wraps around the Pt(0) center in a pseudo-chair conformation, enabling an almost perfect trigonal-planar arrangement. The Pt−carbene distance is 2.067(4) Å. The plane formed by the alkene coordinated to platinum and the plane of the imidazole ring are tilted by −51.2(4)°. The olefinic bond lengths are 1.427(8) and 1.436(7) Å, indicating extensive back-bonding of the electron-rich Pt(0) center onto the π^* of the alkenes. These features are in line with the closely related (IPr)Pt(dvtms) derivative.[13]

Initial attempts to generate $Pt(alkene)_3$ complexes with monodentate alkenes, using our method, proved unsuccessful, and precipitation of Pt black readily occurred during the reduction. It is likely that these complexes are too unstable in solution at 60 °C. Thus, our method is complementary to Stone's reduction with $Li_2(cot)$. Preliminary experiments suggest that the reduction process presented here is also applicable to palladium and nickel, but the low stability of the resulting complexes renders their isolation difficult and manipulations must be carried out with the rigorous exclusion of oxygen.

Conclusions

We have devised an efficient and operationally simple two-step process for the formation of (L)Pt(η^4-1,6-diene) complexes from commercially available $H_2PtCl_6{\cdot}xH_2O$. Our approach led us to expand the scope of the reduction process involved in the formation of Karstedt's catalyst to dienes other than dvtms. The variation of the diene fragment enables the straightforward modulation of the stability of the resulting complex and the ease with which the L−Pt(0) fragment is generated. This method should find applications in the generation of new Pt(0) complexes and should expand the scope of catalytic processes employing the reactive L−Pt(0) fragment.

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Supporting Information Available: Detailed experimental procedures, complete characterization of the complexes including ^{1}H and ^{13}C NMR spectra, and crystallographic data for **4**, including atomic coordinates, displacement parameters, bond lengths, and bond angles, as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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