

Coordination insertion reactions of acrylonitrile into Pd–H and Pd–methyl bonds in a diimine-palladium(II) system

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Abstract

Acrylonitrile (AN) displaces the ethyl ether ligand of the cationic complex $[\text{Pd}(\text{N-N})\text{Me}(\text{Et}_2\text{O})]^+$ ($\text{N-N} = (2,6\text{-}(i\text{-Pr})_2\text{C}_6\text{H}_3)\text{-N}=\text{CMeCMe}=\text{N-(2,6-(}i\text{-Pr})_2\text{C}_6\text{H}_3)$) to form the N-bonded AN complex $[\text{Pd}(\text{N-N})\text{Me}(\text{AN})]^+$, which exists as two interconverting rotamers. On standing or heating, $[\text{Pd}(\text{N-N})\text{Me}(\text{AN})]^+$ undergoes 2,1-insertion to give $[\text{Pd}(\text{N-N})(\text{CH}(\text{CN})\text{CH}_2\text{Me})(\text{AN})]^+$, which undergoes β -hydrogen elimination to give the intermediate hydride, $[\text{Pd}(\text{N-N})\text{H}(\text{AN})]^+$, which in turn inserts AN to give the cyanoethyl complex $[\text{Pd}(\text{N-N})(\text{CH}(\text{CN})\text{Me})]^+$. Dimerization of the $[\text{Pd}(\text{N-N})(\text{CH}(\text{CN})\text{CH}_2\text{CH}_3)]^+$ moiety via bridging nitrile groups also occurs, giving the dicationic species $[\text{Pd}(\text{N-N})(\text{CH}(\text{CN})\text{CH}_2\text{Me})]_2^{2+}$. Although $[\text{Pd}(\text{N-N})\text{Me}(\text{AN})]^+$ does behave as a typical Brookhart ethylene polymerization catalyst, it does not catalyze AN polymerization and in fact added AN suppresses ethylene polymerization.

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1. Introduction

Although there have in recent years been numerous investigations into the use of group 4 metallocene complexes, of the type $[\text{Cp}'_2\text{MR}]^+$ ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$; $\text{R} = \text{alkyl}$; $\text{Cp}' = \text{substituted cyclopentadienyl}$), as homogenous catalysts for the coordination (Ziegler) polymerization of olefins [1], this class of compounds has not normally been found useful for either the homopolymerization of polar olefins such as acrylates, methacrylates, vinyl halides and vinyl amines or for the copolymerization of these monomers with e.g. ethylene or propylene [2]. In general, it seems, the Lewis base sites of all such candidate monomers coordinate preferentially to the highly Lewis acidic metal ions, thus precluding η^2 -coordination and the migratory insertion processes necessary for coordination polymerization. Where polymerization of, e.g., methyl methacrylate

has been found to be induced by cationic metallocene species, the mechanism involves not coordination polymerization but rather a group transfer process [3].

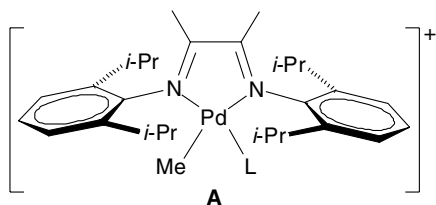
While many polar monomers are readily polymerized via radical and ionic processes [4], the resulting polymeric products are generally atactic in nature and no highly stereoselective procedures giving largely iso- or syndiotactic materials are as yet available. In addition, since ethylene and propylene are not readily polymerized via radical or ionic processes, there are as yet no generally satisfactory routes to the formation of linear ethylene- or propylene-polar monomer copolymers. Given the properties which materials of these types are expected to exhibit [1c,2a,5], it is not surprising that research in this area has been intense.

One potential solution to the problem of coordination of a polar monomer via the Lewis base site is to utilize relatively weakly electrophilic metal complexes, and considerable research has been carried out with late metal catalysts, especially of palladium [6]. Cationic α -diimine complexes of the type $[\text{PdMe}(\text{L})(\alpha\text{-diimine})]^+$

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(A: L = solvent, neutral ligand), which are effective catalysts for the polymerization of ethylene, also catalyze the copolymerization of ethylene with acrylates and methacrylates [6].



However, the efficacies of such catalyst systems are affected adversely by the inclination of incorporated ester-containing units to coordinate to the metal, thus decreasing catalytic activity significantly. Attempts to use similar catalysts to polymerize vinyl chloride also resulted in an initial 1,2-vinyl chloride insertion into the Pd–methyl bond, but the thus formed Pd–CH₂CHClMe species undergoes facile β -chloride migration to the metal to form propylene and catalytically inactive chloropalladium compounds [7].

Given the at least partial functional group tolerance of compounds of type A, we were interested in investigating the chemistry of such a diiminepalladium(II) complex with the polar monomer acrylonitrile (AN). The commercially important material hydrogenated acrylonitrile-butadiene rubber (HNBR) is formed by the radical co-polymerization of AN with 1,3-butadiene followed by hydrogenation of the backbone C=C bonds [8]. HNBR is in effect a copolymer of AN with ethylene, and a direct coordination polymerization route to AN–ethylene co-polymers is therefore very desirable.

Computational investigations suggest that palladium complexes of type A, where L = AN prefer σ -coordination via nitrogen over π -bonding via the C=C bond (henceforth η^2 -coordination) of AN by about 13 kcal/mol, although interestingly the calculated barrier for insertion of η^2 -coordinated AN is similar to that of ethylene [9]. However, these computed relative energies are very sensitive to the nature of the coordinated ligands [9c], and it seems quite possible that the effects of changing ligands, solvents and/or counteranions could reduce the preference for N-coordination by a sufficient amount that coordination polymerization processes involving AN could become feasible. Furthermore, complexes of type A, where L = AN and aryl nitriles have been used as catalysts for the copolymerization of ethylene and 1-alkenes with methyl methacrylate, implying that substitution of N-bonded nitriles by olefins in this system is facile [6d], and it has long been known that even such weakly coordinating alkenes such as isobutene, pinene, camphene and styrene readily displace the benzonitrile ligands from PdCl₂(PhCN)₂ to give alkene complexes of the type [PdCl₂(alkene)]₂ [10]. We note also that, in

contrast to the situation with vinyl chloride where facile β -chloride migration occurs to give a catalytically inactive species [7], β -cyano migration in a species of the type Pd–CH₂CH(CN)Me would probably be much less facile because of the greater bond strength of the C–CN bond (~132 kcal/mol) than of the C–Cl bond (~94 kcal/mol) [11].

We have been investigating the chemistry of AN with [Pd{(2,6-(*i*-Pr)₂C₆H₃)-N=CMeCMe=N-(2,6-(*i*-Pr)₂C₆H₃)}Me(OEt₂)] [B{(3,5-(CF₃)₂C₆H₃)₄}] (1), a complex of type A (L = Et₂O) and a very active catalyst for ethylene, propylene and 1-hexene polymerization [6b]. We find that the ethyl ether of 1 is readily substituted by AN to give the isolable AN complex [Pd(N–N)Me(AN)] [B{(3,5-(CF₃)₂C₆H₃)₄}] (2), and that the latter reacts further to give new complexes which contain inserted AN molecules. As this work was being completed, Wu et al. reported [12a] a somewhat similar but more extensive study of the AN coordination and insertion chemistry of 2 and related cationic complexes while Groux et al. reported [12b] a complementary study of neutral and anionic complexes. However, while the former report is especially relevant to this work, the focus is quite different. Whereas Wu et al. [12a] broadly investigate the room temperature insertion and coordination chemistry of a series of six cationic complexes, of which compound 2 receives virtually no attention, our work is focused specifically on 2. We report two novel and unprecedented observations for this type of compound, that the N-bonded AN ligand exists in solution as two interconverting rotamers and that ring current effects of the aryl rings of the diimine ligand generate unusual and heretofore unnoted chemical shifts of the other coordinated ligands. We also impose relatively forcing reaction conditions on 2, thereby inducing and observing previously unreported AN insertion chemistry, and we investigate the influence of AN on ethylene polymerization by this catalyst system. Henceforth, the diimine ligand (2,6-(*i*-Pr)₂C₆H₃)-N=CMeCMe=N-(2,6-(*i*-Pr)₂C₆H₃) will be designated as N–N, [B{(3,5-(CF₃)₂C₆H₃)₄}] as [BAR'₄].

2. Experimental

All reactions were carried out under purified argon using standard Schlenk line techniques. Dichloromethane was dried by passing through a dried alumina column, CD₂Cl₂ over calcium hydride and DMSO-*d*₆ over 4A molecular sieves. All ¹H NMR spectra were run on a Bruker AV500 spectrometer, chemical shifts being referenced to TMS via the residual proton signals of the deuterated solvents. Electrospray mass spectrometry (ESMS) experiments were run in positive and negative ion modes on Quattro VG and Applied Biosystems/MDS Sciex QSTAR XL instruments at a cone

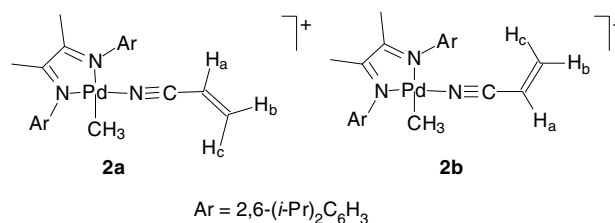
voltage typically of 20 V; nitrogen was used as the nebulizing gas, CH_2Cl_2 as the carrier solvent. The ions were in all cases complex multiplets, and the m/e values quoted below are for the strongest line in each multiplet. Elemental analyses were carried out by Canadian Microanalytical Services of Delta, BC, and molecular mechanics calculations were carried out using PCModel version 8.0 (Serena Software, Bloomington, IN). Acrylonitrile was purchased from Aldrich and purified of moisture and inhibitor by stirring over CaH_2 for a day; it was then vacuum distilled into a Schlenk tube and stored in a refrigerator (3 °C). The compound $[\text{Pd}(\text{N-N})\text{Me}(\text{OEt}_2)]^+[\text{BAR}'_4]^-$ was prepared as in the literature [6b].

Synthesis of 2. A solution of 200 mg of $[\text{Pd}(\text{N-N})\text{Me}(\text{OEt}_2)]^+[\text{BAR}'_4]^-$ (0.137 mmol) in 2 mL AN was stirred under argon for 1 h. The AN was then removed to give a dark orange/brown oil, which was washed with hexanes and dried under reduced pressure to give a yellow solid. This was washed by repeated extractions with hexanes, and was dried overnight under reduced pressure. Yield: 177 mg, 90%. ^1H NMR (CD_2Cl_2 , 298 K) δ 7.74 (s, 8H, $\text{BAR}'_4\text{H}_o$), 7.58 (s, 4H, $\text{BAR}'_4\text{H}_p$), 7.43 (m, 2H, H_{aryl}), 7.37 (m, 4H, H_{aryl}), 6.22 (d, 1H, $^3J(\text{HH}) = 12$ Hz, CHHCHCN), 5.84 (d, 1H, $^3J(\text{HH}) = 18$ Hz, CHHCHCN), 5.44 (dd, 1H, $^3J(\text{HH}) = 12$, 18 Hz, CH_2CHCN), 2.92 (m, 4H, CHMe_2), 2.26 (s, 3H, $\text{N}=\text{CCH}_3$), 2.24 (s, 3H, $\text{N}=\text{CCH}_3$), 1.38 and 1.26 (m, 12H each, $\text{CH}(\text{CH}_3)_2$), 0.58 (s, 3H, PdCH_3). Anal. Calc. for $\text{C}_{64}\text{H}_{58}\text{BF}_{24}\text{N}_3\text{Pd}$: C, 53.29; H, 4.05; N, 2.91. Found C, 53.21; H, 4.07; N, 2.80%.

Reactions of 2 with acrylonitrile. In a typical reaction, 35–45 mg of **2** were dissolved in 1 mL of AN and the solution was stirred under argon (a) at room temperature for 12 h, (b) at 50 °C for 2 h, or (c) at reflux (77 °C) for 12 h. As polyacrylonitrile was formed in (c), a blank run, in the absence of **2**, was also run. In all cases, the AN was then removed under reduced pressure and the resulting oily materials were washed with hexanes, dried overnight under vacuum and characterized by ^1H NMR spectroscopy and ESMS.

3. Results and discussion

Synthesis and structure of 2. Dissolution of the orange complex **1** in AN resulted in an immediate color change to yellow, suggesting displacement of the ether by AN to produce the cationic nitrile complex $[\text{Pd}(\text{N-N})\text{Me}(\text{AN})]^+$ (**2**). After stirring for 1 h, the solvent was removed under reduced pressure and the resulting yellow powder was shown by ^1H NMR spectroscopy, ESMS and elemental analyses to be $[\text{Pd}(\text{N-N})\text{Me}(\text{AN})]^+[\text{BAR}'_4]^-$ which may exist in two conformations, **2a** and **2b** (to be discussed below).



The molecular ion of **2** (578 Da) was readily observed in an ES mass spectrum, the isotope pattern of the molecular ion agreeing closely with a calculated spectrum and clearly confirming the formulation of the complex as a coordination complex in which AN had replaced the ether ligand of **1**. Carrying out the reaction of **1** with AN in dichloromethane or ethyl ether resulted in the same product being formed.

Wu et al. [12a] have recently prepared (via the reaction of $\text{Pd}(\text{N-N})\text{MeCl}$ with $[\text{Li}(\text{Et}_2\text{O})_{2.8}][\text{B}(\text{C}_6\text{F}_5)_4]$) but not isolated the analogous compound $[\text{Pd}(\text{N-N})\text{Me}(\text{AN})][\text{B}(\text{C}_6\text{F}_5)_4]^-$, containing the same cation but a different anion. Aside from the additional $[\text{BAR}'_4]^-$ resonances in the ^1H NMR spectrum of **2**, the room temperature NMR spectra of the two compounds compare well. Wu et al. [12a] and Groux et al. [12b] have also identified in solution a number of similar Pd–AN complexes, but in all cases, 2,1-insertion of the AN into the Pd–Me bond occurred relatively rapidly and no cationic AN complexes were actually isolated.

The olefinic chemical shifts in a room temperature ^1H NMR spectrum of **2** are informative with respect to structure. On coordination, the resonance of H_a shifts upfield from δ 5.71 in free AN to δ 5.45 (0.26 ppm), that of H_b downfield from δ 6.09 to δ 6.21 (0.12 ppm) and that of H_c upfield from δ 6.22 to δ 5.85 (0.37 ppm). These coordination induced changes are very different from those of known η^2 –AN complexes of metals in the +2 oxidation state [13], as well as those of the analogous η^2 –propene complex (**A**, $\text{L} = \text{MeCH}=\text{CH}_2$); in these, all three vinyl hydrogen resonances shift upfield by 0.75 ppm or more [6b]. In view of these observations, in addition to the above mentioned computational results [9], we conclude that the AN of **2** is σ -coordinated via the nitrogen of AN. This conclusion is further supported by the nitrile stretching frequency shifting by 49 cm^{-1} to a higher frequency in the IR spectrum [14].

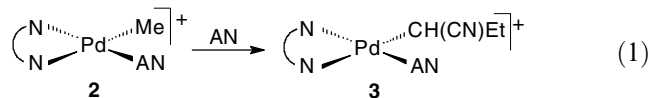
Interestingly, variable temperature NMR studies of **2** suggest that this complex exists in solution as a mixture of at least two interconverting, isomeric forms. Reducing the temperature from 298 to 193 K results in reversible changes in the NMR spectrum, the Pd–methyl resonance and the resonances of H_b and H_c shifting upfield by 0.2, 0.07 and 0.3 ppm, respectively, although the resonances of H_a and the diimine ligand change relatively little.

We rationalize these observations in terms of rapid interconversion between two or more conformations with different chemical shifts. Molecular mechanics (MM) calculations suggest that, because of the steric requirements of the bulky isopropyl groups, the plane of the coordinated AN ligand prefers to be positioned approximately in the molecular plane. Two such conformations are possible, one with H_c approximately eclipsing the Pd–methyl group (**2a**), the other with H_a approximately eclipsing the Pd–methyl group (**2b**; shown as a space filling model in Fig. 1). In the latter, H_c would interact with the π face of the aryl ring and hence experience significant shielding because of ring current effects [15]. Indeed, our MM calculations suggest that conformation **2b** represents the energy minimum, with close contacts between H_c and several of the ring carbon atoms. Such is not the case for H_a and H_b in either conformation, and thus changing the relative populations of the possible conformations would result in the greatest ring current effects being on the chemical shift of the resonance of H_c , which is indeed observed. Increasing the population of **2b** apparently results in an enhanced rate of rotation about the Pd–N bond and increases in the population of rotamers other than that shown in Fig. 1, resulting an upfield shift of the resonance of H_c . Thus, the observed temperature effects on the chemical shift of H_c suggests that **2b** is the more stable rotamer, consistent with the MM calculations.

Reactions of 2 with AN. Although solutions of the $[B(C_6F_5)_4]^-$ salt of **2** are reported to be stable with respect to insertion at 23 °C for several days [12a], we find that compound **2** does in fact engage in insertion reactions within hours in the presence of free AN and that secondary reactions occur under more forcing conditions. Interestingly, reactions in which **2** was stirred in neat AN either at room temperature for 12 h or at

50 °C for 2 h gave yellowish powders whose NMR spectra and ES mass spectra were very similar. Thus, the 1H NMR spectra of both products exhibited, in addition to the resonances of unreacted **2**, a new set of olefinic resonances at δ 6.32 (d, $J = 12.1$ Hz), apparently corresponding to H_b of a second AN complex, and a new H_a resonance at $\delta \sim 5.45$ (m, confirmed by a COSY experiment). The new H_c resonance overlaps exactly with the analogous resonance of **2** at δ 5.85 (confirmed by relative integrations and by a COSY experiment). There were also new ligand resonances in the region δ 1.0–3.3 and several new resonances in the region δ 0–1.0 (an apparent singlet Pd–Me resonance at δ 0.42, a 1:2:1 triplet at δ 0.23, a partially obscured multiplet at $\sim \delta$ 0.41 and multiplets at $\sim \delta$ 0.8–0.9). Thus, the reactions clearly produced complex mixtures.

ES mass spectra were run in an attempt to identify the species in solution, and the mass spectra of the two product mixtures were also found to be similar. In addition to the molecular ion of **2** at 578 Da, both mass spectra exhibited singly charged ions at 592, 631 and 647 Da and several doubly charged ions (~ 553 , ~ 564 , ~ 572 and ~ 586 Da), characterized by their 0.5 Da spacings and very different isotope distribution patterns. Although the assignments of the doubly charged species are as yet unclear, the weak ion at 631 Da corresponds to the mass of a cation of stoichiometry $[Pd(N-N)(CH_2CHCN)_2Me]^+$, containing two AN units in addition to the basic $[Pd(N-N)Me]^+$ moiety. The complex presumably results from insertion of an AN unit followed by coordination of a second N-bonded AN to give a complex such as $[Pd(N-N)(CHCNCH_2Me)(CH_2CHCN)]^+$ (**3**) (Eq. (1)).



A number of similar cationic species have been reported recently, and all involve 2,1-insertions to give 1-cyanopropyl complexes for which $\delta(\text{CH}) = 1.7\text{--}2.8$ (m), $\delta(\text{CH}_2) = 1.0\text{--}1.7$ (m) and $\delta(\text{Me}) = 0.65\text{--}1.00$ (t) [12a]. While the spectra obtained here were obscured in the range δ 1.0–3.3 by very intense diimine resonances, both did exhibit a 1:2:1 triplet at δ 0.23. We tentatively assign this triplet and the new set of AN olefinic resonances to **3**, and thus the NMR and ESMS data are consistent with **3** being the product of a 2,1-insertion of AN. A chemical shift of δ 0.23 is highly unusual for the methyl group of a 1-cyanopropyl ligand [12a], but may be rationalized on the basis of ring current effects as discussed above for compound **2**. Similar upfield shifts have been reported for propylene insertion products of the type $[Pd(N-N)(CH_2=CHMe)(CHMeCH_2)_nMe]$ [6b] and, although not commented on at the time, may possibly be rationalized in the same way. In contrast, the series of analogous complexes by Wu et al. [12a] and

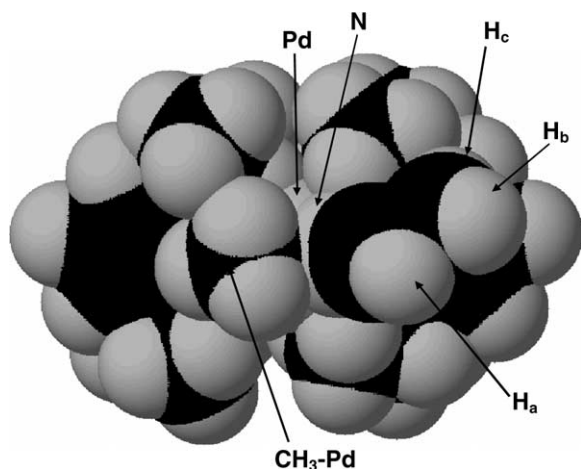
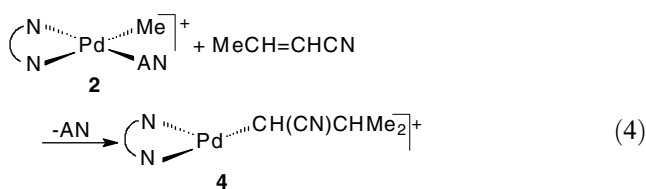
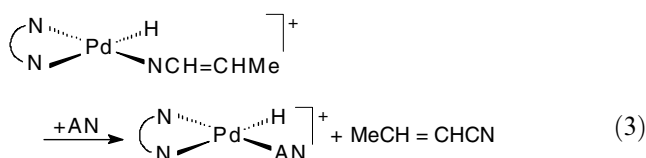
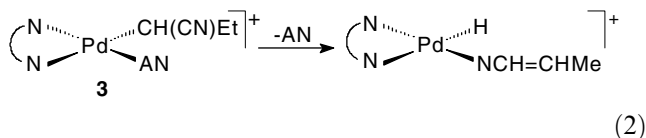


Fig. 1. Space filling model of **2** showing how H_c lies close to an aryl ring in the preferred conformation **2b**. The Pd and nitrile N atoms and the Pd– CH_3 group are labeled to assist in orientation of the viewer.

Groux et al. [12b], in which there are no ligands which can induce ring current effects, exhibit normal chemical shifts for the methyl group of the 1-cyanopropyl ligands.

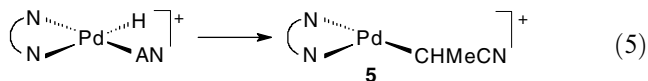
The medium intensity ion at 592 Da exhibits an isotope pattern appropriate for a complex of the stoichiometry $[\text{Pd}(\text{N-N})(\text{C}_4\text{H}_5\text{N})\text{Me}]^+$ (**4**; $\text{C}_4\text{H}_5\text{N} = \text{crotononitrile}$, $\text{MeCH}=\text{CHCN}$). Crotononitrile is the product of β -hydrogen elimination from complex **3** (Eq. (2)), and the formation of **4** must involve release of the coordinated crotononitrile followed by substitution by it of the AN of a molecule of **2** (Eqs. (3) and (4)).



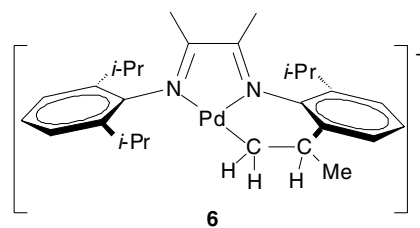
It is difficult to convincingly rationalize the conversion of **2–4** in the presence of excess AN, but crotononitrile does have a much higher boiling point (120 °C) than does acrylonitrile (77 °C) and its relative concentration would increase as the volatiles were removed during workup. In any case a high resolution ES mass spectrum was run to obtain an exact mass for the peak at 592 Da and the experimental value, 592.2903 Da, differed by only 3.3785 ppm from the calculated value for $\text{C}_{33}\text{H}_{48}\text{N}_3\text{Pd}$, 592.2882 Da. No other reasonable stoichiometry was within 17 ppm of the experimental value, and thus attribution of the multiplet at 592 Da to **4** seems firm. Since we observed no unexplained resonances in the olefinic region of the NMR spectrum, it seems likely that **4** contains an inserted $\text{C}_4\text{H}_5\text{N}$ moiety, as in $[\text{Pd}(\text{N-N})(\text{CHCNCHMe}_2)]^+$ (Eq. (4)). It is possible that the vacant site on the metal is occupied by an agostic interaction with one of the *i*-Pr groups or with a methyl of the CHCNCHMe_2 group; ring strain would seem to rule out chelation via the nitrile group.

The initially formed palladium-containing product of β -hydrogen elimination from **3** (Eq. (2)) would be the hydride complex $[\text{Pd}(\text{N-N})(\text{C}_4\text{H}_5\text{N})\text{H}]^+$, isomeric with **2** and hence indistinguishable on the basis of mass spectrometry. A secondary product, $[\text{Pd}(\text{N-N})(\text{AN})\text{H}]^+$, would arise from substitution of the crotonitrile by AN (Eq. (3)), and a weak peak in the ES mass spectrum at 564 Da may be taken as evidence for the presence of

this species although a close examination of the ^1H NMR spectra in the region δ 0 to -20 revealed no hydride resonance. Thus, the species in solution may well be the insertion product, $[\text{Pd}(\text{N-N})(\text{CHCNMe})]^+$ (**5**, Eq. (5)), again with the vacant site on the metal occupied by an agostic interaction as with **4**.



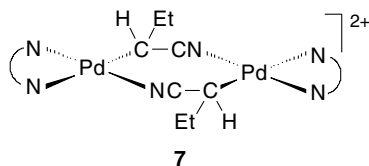
A reaction was also carried out in which **2** was refluxed in neat AN (77 °C) for 12 h and the resulting mixture worked up as above. The ^1H NMR spectrum of the products formed under these much more forcing conditions exhibited many resonances in the region δ 1.0–3.3, suggesting the presence of a complex mixture. Interestingly, there were no resonances in the olefinic region and the above mentioned triplet at δ 0.23 and multiplet (now seen to be a triplet) at δ 0.41 and were much more apparent while the singlet at δ 0.42 had disappeared. The ES mass spectrum exhibited multiplets at 509 (m), 564 (m), 578 (s), 598 (w), 605 (w), 631 (w), 649 (w) and 663 (w) Da, in addition to several others at higher masses. The multiplet at 509 Da exhibited an isotope pattern consistent with its formulation as **6**, i.e., a compound in which metallation of one of the isopropyl groups has occurred. This multiplet was not present in the mass spectra of the reaction mixtures obtained under less forcing conditions, and thus is probably a product of decomposition. As with **4** and **5**, it is possible that the vacant site on the metal is occupied by an agostic interaction.



The peak at 564 Da, attributed above to **5**, is much stronger than it is in the mass spectra discussed above. Again the ^1H NMR spectrum of the reaction mixture exhibited neither hydride nor olefinic resonances, and thus this species seems best formulated as the product of insertion. The multiplet at 631 Da has been discussed above, but those at 649 and 663 Da remain unidentified.

Interestingly, while the main set of peaks of the multiplets at 578, 598 and 631 Da exhibit the isotope patterns expected, all also contain sets of weaker peaks at masses differing from those of the main peaks by 0.5 Da and exhibiting the isotope patterns expected for the corresponding, dicationic dimers. Since the ^1H NMR spectrum of the reaction mixture showed clearly

that the molecules in solution did not contain coordinated AN, the new species must be dimeric, as in **7**.



Thus, dicationic, dinuclear species are readily formed in this system and probably involve bridging nitrile ligands as shown; similar results have been observed elsewhere and, in fact, dinuclear species have been shown to be a common secondary product following 2,1-insertion of AN into a Pd–Me bond [12]. We therefore tentatively assign the second methyl triplet resonance in the NMR spectrum to the dimer **7**.

The question arises then as to whether the monomeric complexes exist in solution or whether they are formed via dimer dissociation within the mass spectrometer. This question cannot be answered, of course, but ES mass spectra of similar platinum complexes have been shown to reflect the species in solution [16a], and the monomeric species may well be stabilized by agostic interactions as above. Somewhat similar platinum containing species have been noted elsewhere [16b]. Unfortunately, the identities of many of the species giving rise to the ions detected in the mass spectrum are as yet unknown.

Polymerization reactions involving 2. Interestingly, it was found that trace amounts of polyacrylonitrile were formed during the 12 h reflux reaction; a ¹H NMR spectrum of the resulting white precipitate in DMSO-*d*₆ exhibited broad resonances at δ 2.1 and 3.2, characteristic of polyacrylonitrile [17]. However, in none of the mass spectra obtained to date have there been any series of peaks separated by 53 Da, as would be expected if multiple insertions of AN at palladium were occurring in this diimine system. Thus, while a single insertion into a Pd–Me or Pd–H bond seems to occur slowly, subsequent insertions appear not to be achievable, a conclusion also reached elsewhere [12]. The small amounts of polyacrylonitrile obtained during the long reflux reaction are presumably a result of radical polymerization processes, possibly initiated by homolysis of Pd–CHC–NEt bonds. Polyacrylonitrile does not form during control experiments, i.e., in the absence of **2**.

However, we have investigated the possibility of ethylene–AN co-polymerization by **2**. Bubbling ethylene through a solution of **2** in CD₂Cl₂ for 2 min results in a color change from yellow to orange, disappearance of the Pd–Me resonance and appearance of the peaks of the type of branched polyethylene reported previously [6b]. The spectrum exhibits no resonance for free ethylene and the diimine resonances are changed very little, but there are vinyl resonances of coordinated acry-

lonitrile and they are shifted upfield slightly from those in the NMR spectrum of **2**. Thus, the resting state in this catalytic system seems to be a complex of the type [Pd(N–N)(AN)(polymeryl)]⁺.

On bubbling ethylene for 3 min through solutions of **2** in several solvents in the presence of a few equivalents of AN, we observe not copolymer formation but rather serious inhibition of ethylene polymerization. The addition of a large excess of AN completely shuts down ethylene polymerization. Complementary experiments in which we attempted to homopolymerize AN in the presence of BPh₃ also failed; the Lewis acidic triarylborane apparently does not bind the nitrogen of the AN sufficiently strongly to allow the olefinic moiety to coordinate preferentially.

4. Conclusions

We have demonstrated that coordination of acrylonitrile in the diimine palladium complex **2** results in formation of complexes **3–7**, in addition to other reactions whose products have not been identified. Trace amounts of polyacrylonitrile are formed under forcing conditions, probably via conventional free radical polymerization initiated by homolysis of the Pd–alkyl bonds of **3** or **4** rather than via coordination polymerization. While **2** does catalyze the coordination polymerization of ethylene, excess acrylonitrile inhibits ethylene polymerization and **2** does not catalyze the copolymerization of ethylene and acrylonitrile.

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