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Reactivity of TCNE or TCNQ Derivatives of Quinonoid Zwitterions: Platinum-Induced HCN Elimination vs Oxidative-Addition

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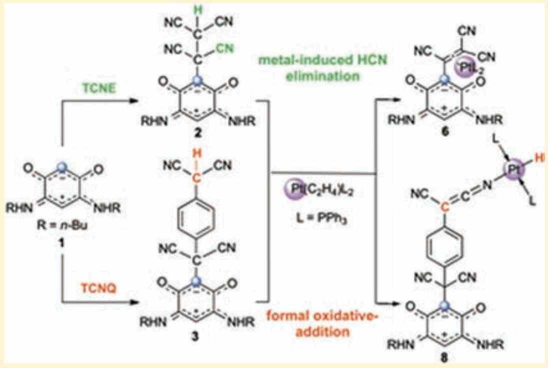
Supporting Information

ABSTRACT: The reaction of the functional, zwitterionic quinonoid molecule (6*E*)-4-(butylamino)-6-(butyliminio)-3-oxo-2-(1,1,2,2-tetracyanoethyl)cyclohexa-1,4-dien-1-olate, [C_6H-2-{$C(CN)_2C(CN)_2H$}]-4,6-(···NH *n*-Bu)$_2$-1,3(···O)$_2$ (**2**), which has been previously prepared by regioselective insertion of TCNE into the C−H bond adjacent to the C···O bonds of the zwitterionic benzoquinone monoimine (6*E*)-4-(butylamino)-6-(butyliminio)-3-oxocyclohexa-1,4-dien-1-olate, C_6H_2-4,6-(···NH*n*-Bu)$_2$-1,3-(···O)$_2$ (**1**), with 2 equiv of [$Pt(C_2H_4)(PPh_3)_2$], afforded the Pt(0) complex [$Pt(PPh_3)_2$(**4**)] (**6**) (**4** = **2**−HCN; (6*E*)-4-(butylamino)-6-(butyliminio)-3-oxo-2-(1,2,2-tricyanoethenyl)cyclohexa-1,4-dien-1-olate), in which a tricyanoethenyl moiety is π-bonded to the metal. A metal-induced HCN elimination reaction has thus taken place. The same complex was obtained directly by the reaction of 1 equiv of the Pt(0) complex [$Pt(C_2H_4)(PPh_3)_2$] with the olefinic ligand [C_6H-2-{$C(CN){=}C(CN)_2$}]-4,6-(···NH*n*-Bu)$_2$-1,3-(···O)$_2$) (**4**), previously obtained by the reaction of **2** with NEt_3 in THF. A similar reactivity pattern was observed between **2** and 2 equiv of the Pd(0) precursor [$Pd(dba)_2$] in the presence of dppe, which led to [Pd(dppe)(**4**)] (**7**), which was also directly obtained from **4** and 1 equiv [$Pd(dba)_2$]/dppe. In contrast to the behavior of the TCNE derivative **2**, the reaction of the TCNQ derivative (6*E*)-4-(butylamino)-6-(butyliminio)-2-(dicyano(4-(dicyanomethyl)phenyl)methyl)-3-oxocyclohexa-1,4-dien-1-olate, [C_6H-2-{$C(CN)_2$*p*-$C_6H_4C(CN)_2H$}]-4,6-(···NH*n*-Bu)$_2$-1,3-(···O)$_2$) (**3**), with 2 equiv of [$Pt(C_2H_4)(PPh_3)_2$] led to formal oxidative-addition of the C−H bond of the $C(CN)_2H$ moiety to give the Pt(II) hydride complex *trans*-[$PtH(PPh_3)_2${$N{=}C{=}C(CN)$*p*-$C_6H_4C(CN)_2$-2-[C_6H-4,6-(···NH*n*-Bu)$_2$-1,3-(···O)$_2$)}] (**8**). The molecular structures of **3**, **4**, **6**·0.5(H_2O), and **8**·3(CH_2Cl_2) have been determined by single-crystal X-ray diffraction.



■ INTRODUCTION

Zwitterionic benzoquinone monoimines of type **1** (Scheme 1) show a remarkable delocalization of their 12 π-electron system, which forms two chemically connected but electronically separated 6π-electron subunits.[1] These potentially antiaromatic molecules have attracted much interest because of their unusual electronic structure,[2−6] their coordination chemistry,[7−15] their ability to form supramolecular arrangements,[8] and the potential applications of their metal complexes in, e.g., optical recording[10] and homogeneous catalysis.[7,9] These zwitterions can behave as noninnocent ligands in Cu[11,12] and Pd[13] chemistry and promote "metal−metal coupling" in Ru[14] and Mo[15] complexes. Furthermore, they have been deposited on gold and ferroelectric lithium niobate surfaces, and molecular films have been obtained which are endowed with interesting physical properties related to their strong dipolar nature.[16,17] Replacement of the R groups can be readily achieved by a transamination reaction, and this provides access to a range of differently functionalized zwitterions.[8,18]

Molecule-based materials are gaining more and more attention because of their possible applications in the fields of molecular electronics and intelligent materials.[19] In this respect, TCNE (tetracyanoethylene) and TCNQ (7,7′,8,8′-tetracyanoquinodimethane) are important molecules, as they are both strong organic electron acceptors which can easily switch between different oxidation states. They find applications in (metal-)organic conductors[20,21] as well as magnetic materials[22] and are used as precursors to charge transfer salts.[23,24] They can undergo π/π stacking,[25−30] act as nonchelating polydentate ligands, offer a variety of coordination sites and bonding modes (σ and π coordination) to metal centers, behave as noninnocent ligands, and form oligonuclear complexes.[31,32] In addition to various reactions with organic[33−41] and organometallic compounds,[42] TCNE and TCNQ can undergo insertion reactions into aromatic C−H bonds.[43−47]

We have recently described a regioselective carbon−carbon bond formation resulting from the reaction between the zwitterionic quinonoids **1** and TCNE or TCNQ, which leads to novel C-substituted zwitterions, (6*E*)-4-(butylamino)-6-(butyliminio)-3-oxo-2-(1,1,2,2-tetracyanoethyl) cyclohexa-1,4-dien-1-olate,

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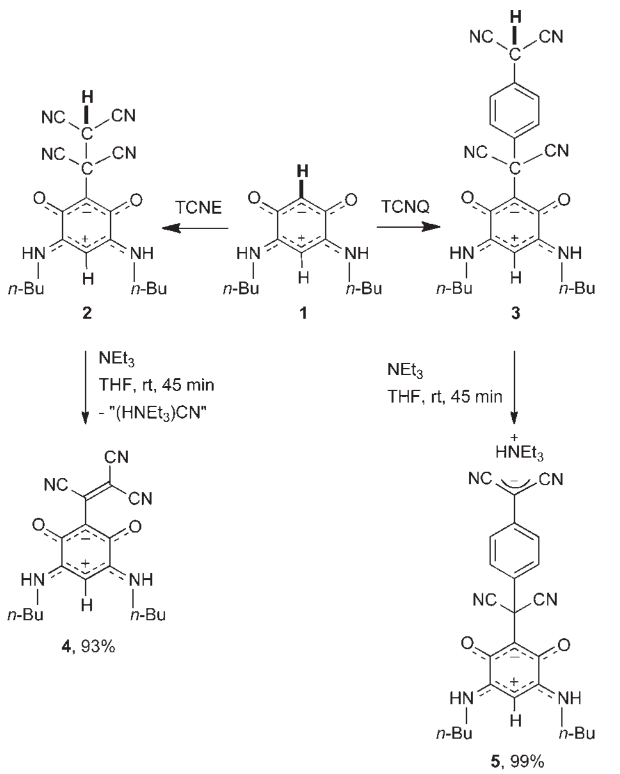
Scheme 1. Regioselective Reactions of Zwitterion 1 with TCNE and TCNQ and Contrasting Behavior of the Products 2 and 3, Respectively, under Basic Conditions[48,49]



[C_6H-2-{C(CN)$_2$C(CN)$_2$H}]-4,6-(···NH n-Bu)$_2$-1,3(···O)$_2$ (**2**), and (6*E*)-4-(butylamino)-6-(butyliminio)-2-(dicyano(4-(dicyanomethyl)phenyl)methyl)-3-oxocyclohexa-1,4-dien-1-olate, [C_6H-2-{C(CN)$_2$*p*-C_6H_4C(CN)$_2$H}]-4,6-(···NH*n*-Bu)$_2$-1,3-(··O)$_2$) (**3**), respectively, by formal insertion of TCNE or TCNQ into the C−H bond of the oxonole moiety (Scheme 1).[48] These reactions provide interesting access to new multifunctional, C-substituted 6π + 6π quinonoid zwitterions, which are potential ligands in coordination chemistry with two (N,O) chelation sites and four cyano groups.

An interesting difference in the behavior of the resulting TCNE- and TCNQ-functionalized zwitterionic benzoquinonemonoimine derivatives **2** and **3** under basic conditions was noted. Thus, HCN elimination from **2** gave the tricyanoethenyl derivative (6*E*)-4-(butylamino)-6-(butyliminio)-3-oxo-2-(1,2,2-tricyanoethenyl)cyclohexa-1,4-dien-1-olate) (**4**), whereas formation of a stable malodinitrile salt, (6*E*)-(4-((5-(butylamino)-3-(butyliminio)-2-oxido-6-oxocyclohexa-1,4-dien-1-yl)dicyanomethyl)-phenyl)dicyanomethanide (**5**), was obtained from **3** (Scheme 1).[49]

One of our objectives in investigating the coordination properties of the functional zwitterions **2**−**4** was to compare the reactivity of the zwitterionic part of the molecules with that of the TCNE- or TCNQ-derived fragment. In the course of our investigations, which will be described here, an unexpected metal-mediated loss of HCN from the TCNE-derivative **2** occurred upon reaction with Pt(0) and Pd(0) precursors, whereas in the case of the TCNQ derivative **3**, formation of a platinum−hydride complex was observed instead. In addition to ligands **3** and **4**, the metal complexes **6** and **8** have been fully characterized, including by X-ray diffraction.

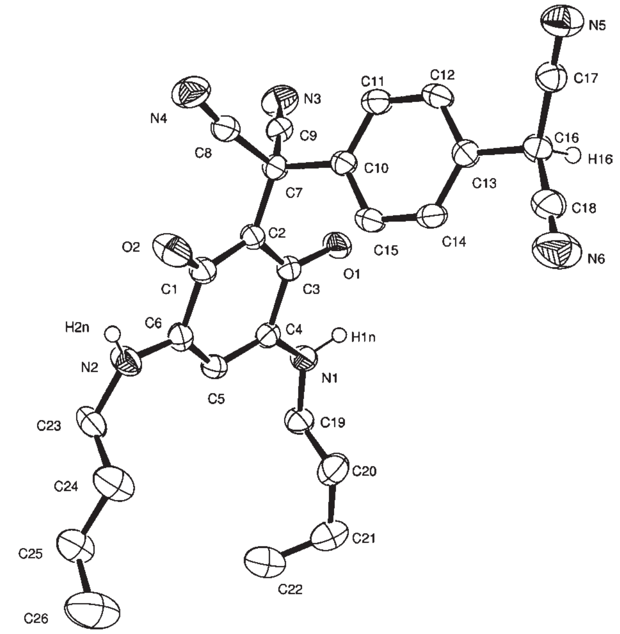


Figure 1. ORTEP of the crystal structure of **3**. Ellipsoids include 50% of the electron density. Only the H atoms on the heteroatoms and at C16 are shown. Selected bond lengths [Å] and angles [deg]: C1−C2 1.396(3), C2−C3 1.405(3), C3−C4 1.518(3), C4−C5 1.393(3), C5−C6 1.385(3), C1−C6 1.520(3), C2−C7 1.526(3), C7−C8 1.497(3), C7−C10 1.551(3), C10−C11 1.381(3), C11−C12 1.381(3), C12−C13 1.382(3), C13−C16 1.531(3), C8−N4 1.133(3), O2−C1−C2 126.0(2), O2−C1−C6 115.9(2), C1−C2−C7 121.9(2), C8−C7−C2 113.58(19), N4−C8−C7 172.6(3), C2−C7−C10 114.69(18), C9−C7−C8 103.97(19), N2−C6−C1 112.5(2), N2−C6−C5 125.7(2).

■ RESULTS AND DISCUSSION

Ligand Synthesis. Compounds **2** and **3** have been prepared recently by reaction of 4,6-diaminoresorcinol dihydrochloride with an excess of *n*-butylamine in water, followed by TCNE or TCNQ insertion into the C−H bond of the oxonole moiety, respectively.[49] The molecular structure of **3** has now been determined by X-ray diffraction (Figure 1). The −C(CN)$_2$-*p*-C_6H_4−CH(CN)$_2$ moiety is attached to the zwitterionic core by a C−C single bond between the carbon atoms C2 and C7. The bond distances and angles for **3** are similar to those reported for analogous TCNQ insertion products.[48] The retention of a zwitterion core is confirmed by the values of the C···O, C···C, and C···N bonds involving the C1−C6 ring, which are intermediate between those for single and double bonds and reflect electronic delocalization. In contrast, the C1−C6 and C3−C4 bond lengths of 1.520(3) and 1.518(3) Å, respectively, correspond to C−C single bonds, which connect the two 6π systems without participating in the electronic delocalization. The bond lengths within the C10−C15 ring are in agreement with those reported for aromatic compounds. The CH(CN)$_2$ and C(CN)$_2$ groups adopt a staggered conformation.

Compound **4** has been previously obtained in high yield from **2** by a NEt$_3$-induced elimination reaction of HCN (Scheme 1).[49] Its molecular structure has now been established by X-ray diffraction and shows that the zwitterionic core displays the characteristic features typical for this class of compounds (Figure 2). The central carbon of the anionic, oxonole moiety

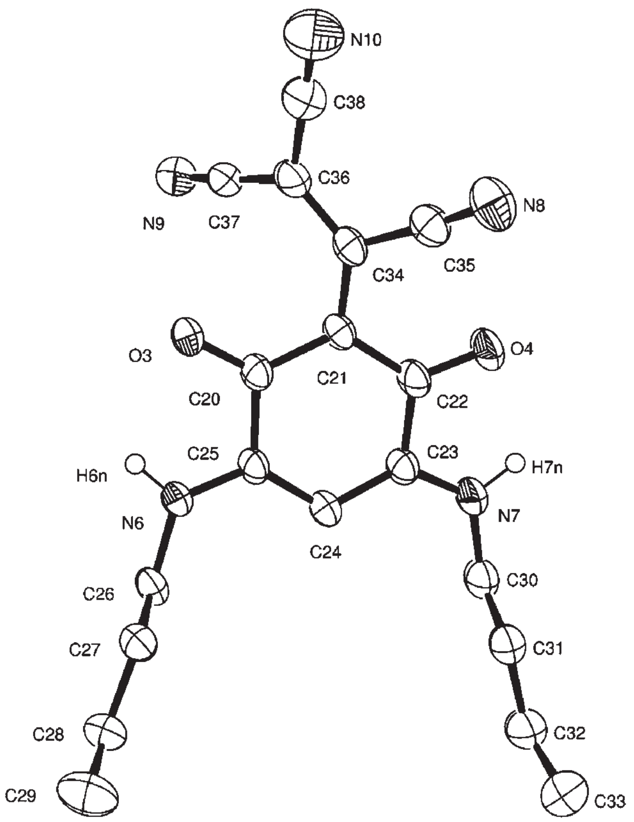


Figure 2. ORTEP of the molecular structure of **4**. Ellipsoids include 50% of the electron density. Only the H atoms on the heteroatoms are shown. Selected bond distances [Å] and angles [deg]: C20−C21 1.434(4), C21−C22 1.428(4), C22−C23 1.505(4), C23−C24 1.392(4), C24−C25 1.391(4), C20−C25 1.520(4), C21−C34 1.426(4), C34−C36 1.374(4); C21−C34−C35 118.5(3), C36−C34−C35 114.2(3), C37−C36−C38 117.0(3).

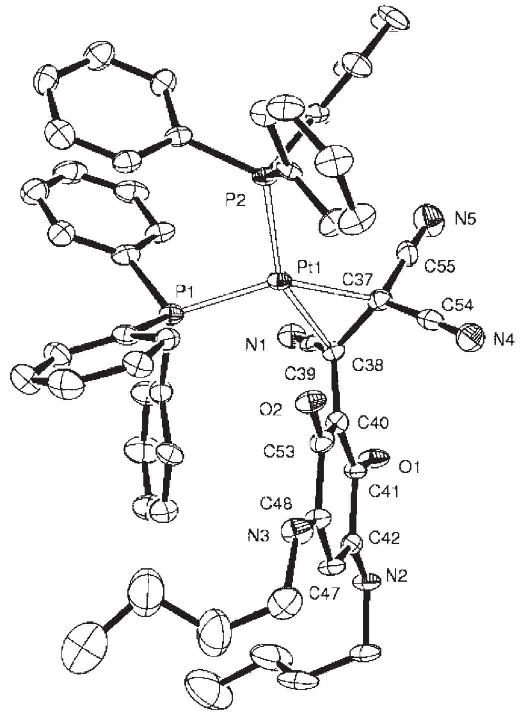
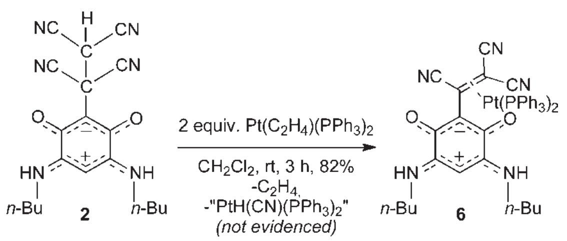


Figure 3. ORTEP of complex **6** in **6**·0.5(H_2O). Displacement ellipsoids are drawn at the 35% level. Hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [deg]: Pt1−P1 2.2618(19), Pt1−P2 2.2913(19), Pt1−C38 2.077(6), Pt1−C37 2.118(6), C37−C38 1.479(10), C38−C40 1.503(9), C38−Pt1−C37 41.3(3), C38−Pt1−P1 104.8(2), C37−Pt1−P1 146.1(2), C38−Pt1−P2 153.8(2), C37−Pt1−P2 112.9(2), P1−Pt1−P2 100.63(7).

Scheme 2. Formation of the Pt Complex 6



of the zwitterion forms a carbon−carbon single bond with a tricyanoethenyl substituent (C21−C34 = 1.426(4) Å). The distance C34−C36 of 1.374(4) Å is in the typical range for cyano-substituted double bonds,[50] as in TCNE (1.354(1)[51] and 1.344(3) Å[52] in the monoclinic and cubic forms, respectively). This is consistent with the ν(C═C) absorption at 1563 cm^{-1}.[50] The plane of the tricyanoethenyl moiety forms an angle of 38.3(4)° with that of the zwitterionic core, in order to minimize steric interactions.

Investigations of the Coordination Properties of 2−4. The coordination chemistry of these ligands was explored toward Pt(0) and Pd(0) reagents, and the anticipated diamagnetic character of the products should enable their characterization by NMR spectroscopy. In order to avoid the formation of coordination polymers, we chose [$Pt(C_2H_4)(PPh_3)_2$] as a metal precursor since after liberation of ethylene, two coordination sites should remain blocked by PPh_3. The reaction of **2** with 2 equiv of [$Pt(C_2H_4)(PPh_3)_2$] in CH_2Cl_2 at room temperature afforded the Pt(0) complex **6** (Scheme 2).

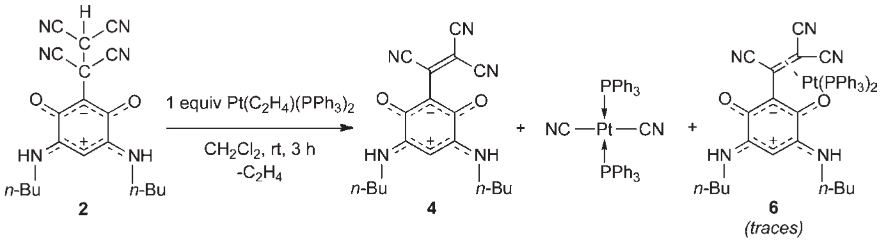
Crystals suitable for X-ray analysis were obtained by slow diffusion of pentane into a saturated solution of **6** in CH_2Cl_2. This reaction has resulted in HCN elimination from **2** to form a complex containing **4** as a ligand. It is noteworthy that this reaction did not affect the quinonoid core of the molecule but only its TCNE-derived moiety. The metal center in **6** is surrounded by two PPh_3 ligands and the C37 and C38 olefinic carbon atoms in such a way that the P1−Pt−P2 and the C37−Pt−C38 planes form an angle of 5.9(2)° (see Figure 3). As expected, the C37−C38 bond distance of 1.479(10) Å is longer than the corresponding one in **4** (1.374(4) Å), which is indicative of M→L π back-donation. It is slightly shorter than in, e.g., [Pt(TCNE)-(PPh_3)$_2$] (1.52 ± 0.03 Å)[53] and is in the range found in complexes with cyano-substituted C═C bonds.[54] Although values above 1.46 Å may be considered as involving C−C single bonds between sp^3-hybridized carbons in a metallacyclic structure,[50] the ν(C═C) absorption at 1594 cm^{-1} in the IR spectrum of **6** suggests retention of a significant double bond character (Table 1). The coordinated olefinic part of ligand **4** is connected to the zwitterionic quinonoid core by the C38−C40 single bond (1.503(9) Å).

When **4** was reacted with only 1 equiv of [$Pt(C_2H_4)(PPh_3)_2$] under otherwise identical conditions, nearly the same yield of **6** was obtained. This leads to the conclusion that in the reaction of Scheme 2, the first equivalent of the metal precursor led to HCN

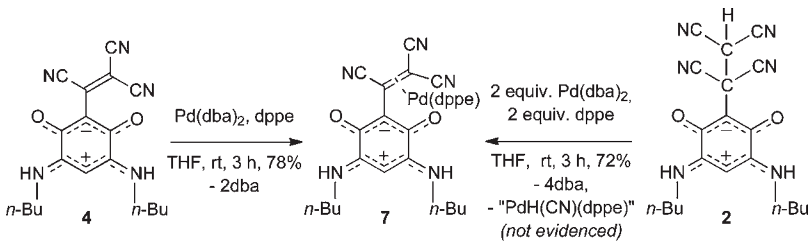
Table 1. Comparison between Ligand 4 and Its Complexes 6 and 7

compound	4	6	7[49]
bond distance $-C(CN){=}C(CN)_2$	1.374(4) (C34−C36)	1.479(10) (C37−C38)	1.482(7) (C15−C17)
ν(C=C) (cm^{-1})	1563	1594	1586
angle between the C−M−C and P−M−P planes		5.9(2)	5.9(2)

Scheme 3. Reaction of 2 with $[Pt(C_2H_4)(PPh_3)_2]$ in a 1:1 Molar Ratio



Scheme 4. Formation of the Pd(0) Complex 7



elimination from **2** in an E2-type process with the formation of a carbon−carbon double bond (formation of $[PtH(CN)(PPh_3)_2]$ is suggested in Scheme 2, but no attempt was made to evidence it). The tricyanoethenyl moiety then coordinated to the second equivalent of the Pt(0) precursor present. This hypothesis was confirmed by the results of the reaction of **2** with only one equivalent of the metal precursor (Scheme 3).

The main reaction product was compound **4**, and traces of **6** were identified by comparison of the ^{1}H NMR spectrum of the reaction mixture with the spectra of the pure compounds.[49] $^{31}P\{^1H\}$ NMR spectroscopy of the crude product and comparison with literature values confirmed the formation of *trans*-$[Pt(PPh_3)_2(CN)_2]$ (δ 14.43, singlet with satellites $^1J(^{31}P,^{195}Pt)$ = 2379 Hz).[55] The protons lost in the reaction are assumed to form dihydrogen, but this was not confirmed.

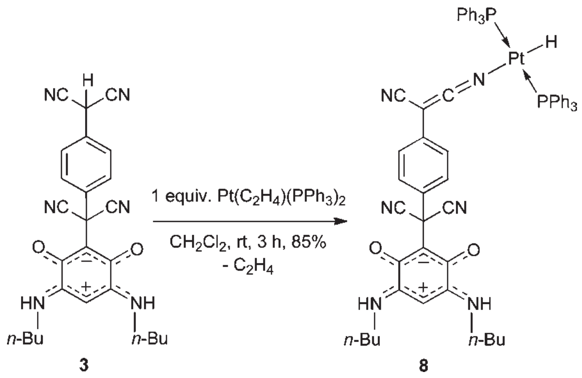
Similar results were obtained in palladium chemistry when **2** was reacted with 2 equiv of $[Pd(dba)_2)]$ in the presence of 1,2-bis(diphenylphosphino)ethane (dppe). This reaction was carried out for 3 h at ambient temperature in THF, and the Pd(0) complex [Pd(dppe)(**4**)] (**7**) was obtained in 72% yield. Starting directly from **4** and 1 equiv of $[Pd(dba)_2]$ and dppe, this complex was obtained in 78% yield (Scheme 4). Complex **7** has been characterized by X-ray diffraction.[49]

Only a few examples have been reported of cyanide loss by HCN elimination from tetracyanoethanyl derivatives. This occurred on silica during chromatography,[56] spontaneously after TCNE insertion into a C−H bond,[57] or by thermal activation.[58] To the best of our knowledge, no metal-induced HCN elimination has been reported previously from a tetracyanoethanyl derivative.

In contrast to the chemistry observed with the TCNE-functionalized zwitterion **2**, the reaction of the TCNQ derivative **3** with $[Pt(C_2H_4)(PPh_3)_2]$ in a 1:1 molar ratio did not lead to HCN elimination but to the formation of the metal hydride complex **8** in 85% yield (Scheme 5). This is probably because elimination of HCN is not favored in **3**,[49] and the system therefore responds differently to **2**, resulting in the formation of a Pt(II) complex. As in the case of **2**, the reaction of **3** with the Pt(0) reagent did not affect the quinonoid core of the molecule.

The structure of the resulting complex **8** in **8**$\cdot 3(CH_2Cl_2)$ was established by X-ray diffraction. The Pt(II) center in **8** has a distorted square-planar coordination geometry defined by two PPh_3 ligands, a ketiminate group derived from ligand **3a** and a H atom (see Figure 4). The angles P1−Pt−P2, N6−Pt−P1, and N6−Pt−P2 are 169.31(7)°, 93.3(2)°, and 96.8(2)°, respectively, and indicate a slightly distorted square planar geometry. The formation of a covalent bond between N6 and Pt is supported by the rather short C24−C26, C26−N6, and N6−Pt distances of 1.376(11), 1.156(10), and 2.067(7) Å, respectively, and by the value of the C26−N6−Pt angle of 171.6(7)°. Consistently, the sum of the angles around the sp^2-hybridized C24 atom is 359.9(7) Å. It is noteworthy that the C24−C26 and C26−N6 bond lengths are similar with those in (α-cyanobenzyl)lithium derivatives (1.38(2) and 1.15(3) Å, respectively).[59] The ^{1}H NMR spectrum of compound **8** contains a triplet at δ −16.47 ppm, owing to coupling with two equivalent P nuclei, flanked with ^{195}Pt satellites, which indicates the presence of a metal hydride. However, this ligand could not be located by X-ray analysis. This resonance and the absence of

Scheme 5. Oxidative-Addition of the TCNQ Derivative 3 to a Pt(0) Complex



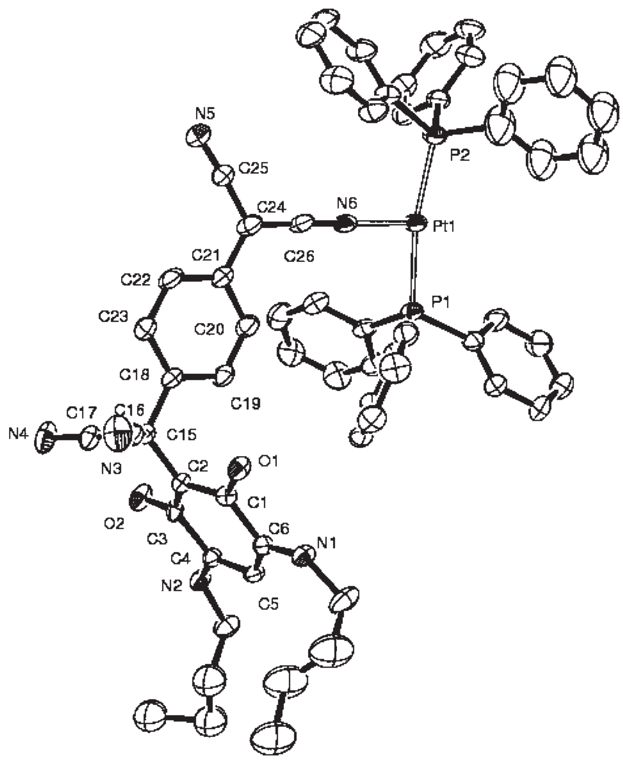


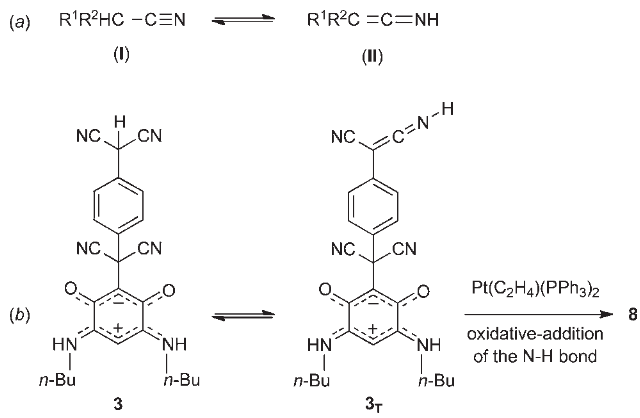
Figure 4. ORTEP of complex $8\cdot 3(CH_2Cl_2)$. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms are omitted for clarity, including those at N1, N2, and Pt. Selected bond distances [Å] and angles [deg]: Pt1−N6 2.067(6), Pt1−P1 2.2839(18), Pt1−P2 2.2872(19), C24−C26 1.376(11), C24−C25 1.406(10), C25−N5 1.155(10), C26−N6 1.156(10), N6−Pt1−P1 93.36(18), N6−Pt1−P2 96.77(18), P1−Pt1−P2 169.31(7), Pt1−N6−C26 171.6(7), C21−C24−C25 120.7(7), C21−C24−C26 121.5(7) C26−C24−C25 117.7(7).

other signals in this spectral range show that only the *trans* isomer is present in solution. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at δ 26.8 ppm, which corresponds to the two *trans* phosphorus nuclei.

Various reaction mechanisms can be considered for the unexpected formation of compound **8** (Scheme 6):

a. An oxidative insertion of the N−H bond of a potential tautomer $\mathbf{3_T}$ of compound **3** across Pt(0) can be envisaged.

Scheme 6. (*a*) Ketenimine Tautomers of Nitrile Compounds and (*b*) Suggested Formation of 8 Involving a Ketenimine Intermediate 3_T



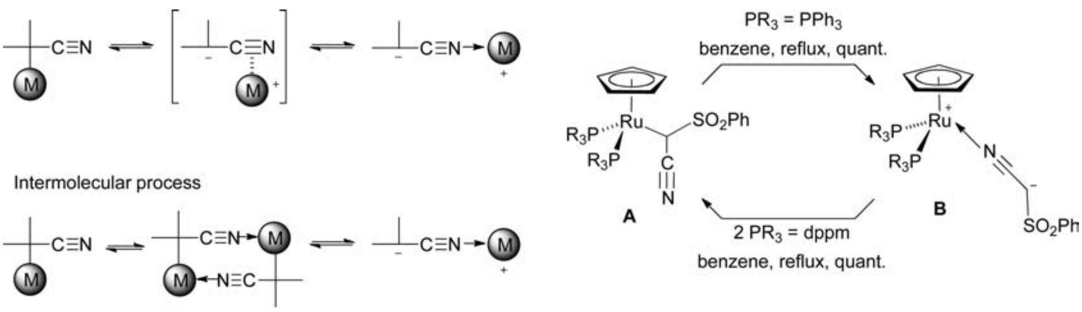
To the best of our knowledge, oxidative-addition reactions of this type have not been described in the literature. In contrast, stable ketenimines (**II**) have been reported to exist, but the tautomeric equilibrium usually favors the nitrile form (**I**). The infrared spectra of ketenimines typically exhibit a characteristic cumulene stretching vibration around 2000−2050 cm^{-1},[60] which was not detected in the spectrum of compound **3**. Nevertheless, an oxidative-addition reaction across Pt(0) of a ketenimine form $\mathbf{3_T}$, potentially present at a concentration below the IR detection limit, cannot be ruled out (Scheme 6).

b. A two-step process involving deprotonation of **3** by the Pt(0) complex acting as a base (thus becoming a Pt(II) hydride species) would form a malodinitrile salt, as in the case of NEt_3 (Scheme 1), and its charge delocalization onto the CN groups α to the carbanion would turn it into a N-ligand for Pt(II).

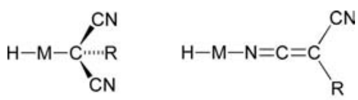
c. Alternatively, oxidative-addition of the $(NC)_2C$−H bond of **3** across the Pt(0) center and subsequent isomerization to compound **8** is also conceivable. Related interconversions between C- and N-bound isomers of ruthenium-bound phenylsulfonylacetonitrile anions have been described by Naota et al.[61] Their work revealed that the C-to-N isomerization process occurs intermolecularly, via a metal slippage over the −C−C≡N π-conjugated unit or, depending on the temperature, via involvement of a μ_2-C,N coordination dimer (Scheme 7). The relative thermal stabilities of the isomers **A** and **B** can be largely controlled by the external ligands PR_3. Furthermore, complexes related to a potential C-coordinated intermediate (**III**) can be found in the literature (Scheme 8). For example, the dicyanomethanide anion $[CH(CN)_2]^-$, which is easily obtained by deprotonation of malonitrile, forms metal complexes related to compound **8**. For these complexes, different bonding modes have been reported. Some mononuclear complexes with C-coordination (**III**)[62] or N-coordination (**IV**)[63] are known, as well as dinuclear complexes exhibiting N,N-[64] and C,N-bridges[65] between two metal centers.

The IR spectra of the C-coordinated complexes (**III**) exhibit typical ν(C≡N) absorption bands at *ca.* 2200 cm^{-1}, whereas in the spectra of the N-coordinated (**IV**) complexes with a

Scheme 7. Isomerization of phenylsulfonylacetonitrile Ru complexes[61]



Scheme 8. C- and N-Coordinated Metal Hydrides Derived from a Dicyanomethanide Group



(III) (IV)

metal−nitrogen bond, bands in the 2120−2150 cm^{-1} range are present. For this potential reaction mechanism, we would expect an insertion reaction of Pt(0) into the C−H bond to occur, followed by a C-to-N isomerization. In the IR spectrum of compound **8**, two absorptions bands are observed at 2189m and 2137s cm^{-1}. We suggest that they correspond to the ν(Pt−H) and the ν(N=C=C) vibrations, respectively. For comparison, the ν(Pt−H) vibration of *trans*-[PtH(Cl)(PPh$_3$)$_2$] at 2220 cm^{-1}[66] shifts to ca. 2180 cm^{-1} in *trans*-[PtH(NO$_2$)(PPh$_3$)$_2$].[67] In addition to the values of these absorptions, our assignment is based on the fact that the Pt−H stretching frequencies in complexes [Pt(H)X(PPh$_3$)$_2$] (X = halogen or CN) are usually of medium intensity, and the ν(N=C=C) absorptions of previously prepared iridium and platinum keteniminato complexes are very intense.[62,68] No evidence for a potential C-coordinated Pt-complex/intermediate could be found, and we assume that the isomerization barrier between a C- and N-coordinated complex could be very low, so that for steric reasons the hypothetical C-coordinated compound would completely isomerize to **8**.

While the TCNQ derivative **3** readily reacted with [Pt(C$_2$H$_4$)(PPh$_3$)$_2$], no reaction occurred with [Pd(dba)$_2$]/dppe at room temperature. When the reaction mixture was heated for 3 h at 50 °C, a reaction occurred, as indicated by a significant color change. However, we failed to characterize the products of this reaction, as they decomposed rapidly.

■ CONCLUSION

Although the already rich coordination chemistry of the potentially antiaromatic zwitterions of type **1**[1,2] has been shown to be due to the presence of chelating N,O donor functions,[7−14] we have observed here that linking a TCNE or a TCNQ fragment to the carbon atom of its oxonole moiety modifies completely the sites of reactivity. Thus, all of the reactions examined in the course of this work took place on the TCNE and TCNQ moieties. An interesting contrast has been observed when comparing the reactivity of zerovalent Pt or Pd metal precursors toward ligands resulting from the selective insertion of TCNE or TCNQ into the C−H bond adjacent to the C···O bonds of the oxonole moiety of the zwitterionic benzoquinonemonoimine C$_6$H$_2$-4,6-(···NHR)$_2$-1,3-(···O)$_2$ (**1**). With the compound derived from TCNE insertion, [C$_6$H-2-{C(CN)$_2$C(CN)$_2$H}]-4,6-(···NH *n*-Bu)$_2$-1,3(···O)$_2$ (**2**), metal-induced HCN elimination, quantitative formation of [C$_6$H-2-{C(CN)=C(CN)$_2$}]-4,6-(···NH*n*-Bu)$_2$-1,3-(···O)$_2$) (**4**) and π-coordination of the tricyanoethenyl moiety of the latter to [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] to afford [Pt(PPh$_3$)$_2$(**4**)] (**6**), were observed. In contrast, with the TCNQ-derived product [C$_6$H-2-{C(CN)$_2$*p*-C$_6$H$_4$C(CN)$_2$H}]-4,6-(···NH*n*-Bu)$_2$-1,3-(···O)$_2$) (**3**), formal oxidative-addition of the C−H bond of the C(CN)$_2$H moiety to give the Pt(II) hydrido, ketiminato complex *trans*-[PtH(PPh$_3$)$_2${N=C=C(CN)*p*-C$_6$H$_4$C(CN)$_2$-2-[C$_6$H-4,6-(···NH*n*-Bu)$_2$-1,3-(···O)$_2$)}] (**8**) occurred. The Pd(0) complex [Pd(dppe)(**4**)] (**7**), analogous to **6**, was also obtained. These different reactivity patterns are due to the presence of the aryl spacer in TCNQ, which does not allow easy formation of the carbon−carbon double bond present in the products derived from TCNE. Similar differences have been observed when **2** and **3** were reacted with NEt$_3$, and this allows one to understand the first steps of their reactions with the zerovalent metal precursors. The olefinic moiety of TCNE and TCNQ is known to undergo π-coordination,[69] e.g., with zerovalent Pt and Pd complexes, which readily react with alkenes to give π complexes.[70−75] Thus, [Pd(PPh$_3$)$_2$(TCNE)] for example has been used as a catalyst precursor in the methoxycarbonylation of styrene,[76] and π-coordination (via CN) of an electron-poor nitrile compound to Pt(0) has been reported.[77,78] Here, we have seen that additional reactivity patterns can be observed when the TCNE or TCNQ moiety is connected to an organic group such as a zwitterionic quinonoid. Obviously, the multifunctional molecules **2** and **3** possess a diversified and sometimes unexpected reactivity toward metal centers, and their coordination chemistry deserves further investigation.

■ EXPERIMENTAL SECTION

General Information. NMR spectra were recorded at room temperature on a Bruker AVANCE 400 ^{1}H NMR (400.13 MHz), ^{13}C NMR (100.61 MHz), and ^{31}P (161.97 MHz) or on a Bruker AVANCE 300 ^{1}H NMR (300.17 MHz), ^{13}C NMR (75.49 MHz), and ^{31}P (121.49 MHz), respectively, and referenced using the residual solvent proton (^{1}H) or solvent (^{13}C) resonance. Mass spectrometric measurements were recorded on a microTOF (Bruker Daltonics, Bremen, Germany) using nitrogen as a drying agent and nebulizing gas. Elemental analyses were performed by the "Service de Microanalyse, Université de Strasbourg" (Strasbourg, France). IR spectra were recorded in the region

Table 2. Data Collection and Refinement Data for 3, 4, $6 \cdot 0.5(H_2O)$, and $8 \cdot 3(CH_2Cl_2)$

compound	3	4	$6 \cdot 0.5(H_2O)$	$8 \cdot 3(CH_2Cl_2)$
chemical formula	$C_{26}H_{26}N_6O_2$	$C_{19}H_{21}N_5O_2$	$C_{55}H_{51}N_5O_2P_2Pt \cdot 0.5(H_2O)$	$C_{62}H_{56}N_6O_2P_2Pt \cdot 3(CH_2Cl_2)$
formula mass	454.32	351.41	1080.05	1428.94
cryst syst	monoclinic	triclinic	triclinic	triclinic
a/Å	8.2246(3)	9.8756(7)	17.483(2)	13.4792(4)
b/Å	22.4335(12)	14.1464(7)	18.137(3)	14.5565(3)
c/Å	15.2684(5)	14.6030(8)	19.762(3)	19.5384(5)
α/deg	90.00	74.673(3)	108.86(2)	98.998(2)
β/deg	120.443(2)	89.656(3)	108.03(2)	107.8050(10)
γ/deg	90.00	79.527(3)	94.15(1)	96.889(2)
unit cell volume/Å^3	2428.73(18)	1932.9(2)	5534.2(18)	3547.25(16)
temp/K	173(2)	173(2)	173(2)	173(2)
space group	$P21/c$	P	$P\bar{1}$	$P\bar{1}$
Z	4	4	4	2
absorption coeff., μ/mm^{-1}	0.082	0.082	2.636	36000
no. of reflns measured	7803	19136	49457	16095
no. of independ. reflns	4493	8789	20563	0.0677
R_{int}	0.0372	0.1215	0.0830	0.0677
final R_1 values ($I > 2\sigma(I)$)	0.0636	0.0898	0.0518	0.0769
final wR (F^2) values ($I > 2\sigma(I)$)	0.1422	0.2229	0.1145	0.1966
final R_1 values (all data)	0.1071	0.1384	0.0944	0.0953
final $wR(F^2)$ values (all data)	0.1675	0.2600	0.1275	0.2055
goodness of fit on F^2	1.123	1.030	0.916	1.047

3500−650 cm^{-1} on a Nicolet 6700 FTIR spectrometer (ATR mode, diamond crystal). Solvents were freshly distilled under argon prior to use. 4,6-Diaminorecorcinoldihydrochloride was purchased from Acros. All reactions for air- and water-sensitive compounds were performed using standard Schlenk techniques under a dry argon atmosphere.

The precursor complexes $[Pt(C_2H_4)(PPh_3)_2]$ and $[Pd(dba)_2]$ were synthesized by literature methods from *cis*-$[PtCl_2(PPh_3)_2]$ and $PdCl_2$, respectively,[79,80] and **1**, **2**, **3**, and **4** were prepared as described.[49]

Synthesis of 6. *Method A.* Solid $[Pt(C_2H_4)(PPh_3)_2]$ (0.278 g, 0.372 mmol) was added to a solution of zwitterion **4** (0.131 g, 0.373 mmol) in CH_2Cl_2 (20 mL), and the resulting mixture was stirred for 3 h at room temperature. Then, all volatile components were removed under reduced pressure, and the remaining solid was washed with pentane and dried under a vacuum to yield compound **6** as a brown solid (0.316 g, 0.295 mmol, 79%).

Method B. The TCNE derivative **2** (0.093 g, 0.24 mmol) and $[Pt(C_2H_4)(PPh_3)_2]$ (0.362 g, 0.484 mmol) were dissolved in CH_2Cl_2 (20 mL). The resulting solution was stirred for 3 h at room temperature and concentrated to about 4 mL, and then pentane was added. The precipitate was collected by filtration and recrystallized from CH_2Cl_2/pentane. After drying under reduced pressure, compound **6** was obtained as a brown solid (0.213 g, 0.198 mmol, 82%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.97 (t, ^3J(H,H) = 7.3 Hz, 6H, CH_3), 1.35−1.47 (m, 4H, CH_2CH_3), 1.63−1.73 (m, 4H, NCH_2CH_2), 3.30 (q, owing to overlap dt, ^3J(H,H) = 6.7 Hz, 4H, NCH_2), 4.94 (s, 1H, N···C···C−H), 7.04−7.50 (m, 30H, aromatic H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 13.71 (CH_3), 20.09 (CH_2), 30.31 (CH_2), 42.90 (CH_2), 80.35 (N···C···C-H), 127.63 (d, ^3J(C,P) = 10.6 Hz, *m*-Ph), 128.19 (d, ^3J(C,P) = 10.4 Hz, *m*-Ph), 129.76 (s, *p*-Ph), 130.01 (s, *p*-Ph), 133.95 (d, ^2J(C,P) = 12.2 Hz, *o*-Ph), 134.24 (d, ^2J(C,P) = 12.1 Hz, *o*-Ph), 155.85 (C···N), 169.46 (C···O) ppm. Not all ^{13}C NMR signals could be observed because of the low solubility of the compound in $CDCl_3$. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 20.35 (d, ^2J(P,P) = 4.9 Hz, with satellites ^1J(P, ^{195}Pt) = 3612 Hz), 21.28 (d, ^2J(P,P) = 5.1 Hz, with satellites ^1J(P,^{195}Pt) = 4310 Hz). IR ν_{max} (pure, diamond orbit)/cm^{-1} 3194brm, 3051w, 2956m, 2929m, 2869w, 2360w, 2342w, 2209m, 1594m, 1535s, 1460s, 1433s, 1397m, 1358w, 1309w, 1287w, 1246w, 1221m, 1185m, 1094s, 1027m, 998m, 911w, 850w, 814w, 769w, 737s, 690vs. MS (ESI): m/z 1094.308 ($[M+Na]^+$). Anal. Calcd for $C_{55}H_{51}N_5O_2P_2Pt \cdot 0.5CH_2Cl_2$: C, 59.86; H, 4.71, N, 6.29. Found: C, 60.66; H, 4.91; N, 6.54.

Synthesis of 7. Zwitterion **2** (0.300 g, 0.793 mmol), $[Pd(dba)_2]$ (0.910 g, 1.583 mmol), and dppe (0.631 g, 1.583 mmol) were dissolved under inert conditions in freshly distilled THF (20 mL). The resulting mixture was stirred for 3 h at ambient temperature. The solvent was evaporated, and the residue was dissolved in about 5 mL of CH_2Cl_2 and precipitated with pentane. The precipitation was repeated twice. The precipitate was collected by filtration, washed with Et_2O and pentane, and dried under reduced pressure. Product **7** was obtained as an orange solid (0.488 g, 0.570 mmol, 72%). This complex has been obtained previously by the reaction of **4** with $[Pd(dba)_2]$, and the analytical and spectroscopic data are identical.[49] $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 13.68 (CH_3), 20.11 (CH_2), 26.40 (m with appearance of t, AA′XX′ system with A = ^{13}C, X = ^{31}P, PCH_2, N = 35.6 Hz with $N = |J(A,X) + J(A,X')|$,[81,82] 26.70 (dd appearance of t, AA′XX′ system with A = ^{13}C, X = ^{31}P, PCH2, N = 36.2 Hz),[81,82] 30.31 (CH_2), 42.97 (CH_2), 80.27 (N···C···CH), 104.92 (d, ^1J(C,P) = 4.0 Hz, NCCCN), 116.75 (s, CN), 116.77 (d, ^3J(P,C) = 2.7 Hz, CN), 116.93 (d, ^3J(P,C) = 7.8 Hz, CN), 128.10 (d, ^3J(C,P) = 9.7 Hz, *m*-C_{dppe}), 128.97 (d, ^3J(C,P) = 10.2 Hz, *m*-C_{dppe}), 129.00 (d, ^3J(C,P) = 10.2 Hz, *m*-C_{dppe}), 130.51 (s, *p*-C_{dppe}), 130.76 (s, *p*-C_{dppe}), 130.95 (s, *p*-C_{dppe}), 131.31 (d, ^1J(C,P) = 34.3 Hz, *ipso*-C_{dppe}), 131.34 (d, ^2J(C,P) = 12.1 Hz, *o*-C_{dppe}), 132.45 ("dd", AA′XX′ system with A = ^{13}C, X = ^{31}P, *ipso*-C_{dppe}, N = 35.6 Hz),[81,82] 132.46 (d, ^2J(C,P) = 14.1 Hz, *o*-C_{dppe}), 133.26 ("dd", AA′XX′ system with A = ^{13}C, X = ^{31}P, *ipso*-C_{dppe}, N = 37.4 Hz),[81,82] 133.80 (d, ^2J(C,P) = 15.2 Hz, *o*-C_{dppe}), 134.05 (d, ^2J(C,P) = 15.2 H, *o*-C_{dppe}), 155.31 (C···N), 169.35 (C···O), 169.41 (C···O) ppm.

Synthesis of 8. Solid $[Pt(C_2H_4)(PPh_3)_2]$ (0.257 g, 0.343 mmol) was added to a solution of zwitterion **3** (0.258 g, 0.343 mmol) in CH_2Cl_2 (30 mL).

The reaction mixture was stirred at room temperature for 3 h. Then, the mixture was concentrated under reduced pressure to about 5 mL, and pentane was added. The precipitate was collected by filtration and dried under a vacuum to give the product as a pink solid (0.343 g, 0.292 mmol, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ −16.47 (t, ^2J(H,P) = 13.2 Hz, with satellites J(H,^{195}Pt) = 522 Hz), 0.97 (t, ^3J(H,H) = 7.3 Hz, 6H, CH_3), 1.39−1.48 (m, 4H, CH_2CH_3), 1.65−1.73 (m, NCH_2CH_2), 3.35 (q owing to overlap dt, ^3J(H,H) = 6.7 Hz, 4H, NCH_2CH_2), 5.19 (s, 1H, N⋯C⋯C−H), 6.15 (AA′ part of an AA′BB′ spin system, 2H, ^3J(H,H) = 8.6 Hz, aromatic C−H), 7.08 (BB′ part of an AA′BB′ spin system, 2H, ^3J(H,H) = 8.7 Hz aromatic C−H), 7.43−7.58 (m, 30H, aromatic C−H), 8.21 (br t, ^3J(H,H) = 5.7 Hz) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 13.54 (CH_3), 20.05 (CH_2), 30.14 (CH_2), 38.34 ($C(CN)_2$, 43.20 (CH_2), 80.94 (N⋯C⋯C-H), 102.50 (O⋯C⋯C), 115.96 (CN), 119.94 (aromatic- CH), 120.93 (C), 122.99 (C), 124.74 (C), 125.88 (aromatic CH), 128.90 (m appearance of a t, AA′XX′ system with A = ^{13}C, X = ^{31}P, *m*-C, N = 10.7 Hz, with $N = |J(A,X) + J(A,X')|$),[81,82] 130.91 (m appearance of a t, AA′XX′ system with A = ^{13}C, X = ^{31}P, *ipso*-C, N = 57.4 Hz),[81,82]131.30 (CH, *p*-C), 134.09 (m appearance of a t, AA′XX′ system with A = ^{13}C, X = ^{31}P, *o*-C, N = 13.6 Hz),[81,82] 138.81 (C), 155.27 (C⋯NH), 167.85 (C⋯O) ppm. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 26.8 (s, with ^{195}Pt satellites $^1J(^{31}P,^{195}Pt)$ = 2961 Hz) ppm. IR ν_{max} (pure, diamond orbit)/cm^{-1}): 3223 w, 2955w, 2189m, 2137s, 1602m, 1538m, 1501m, 1482s, 1435s, 1402m, 1365w, 1312m, 1289m, 1256w, 1227w, 1161w, 1142w, 1098s, 1026w, 998m, 850m, 824m, 750s, 742s, 709s. 690vs. Anal. Calcd for $C_{62}H_{57}N_6O_2P_2Pt\cdot 0.5CH_2Cl_2$: C, 61.70; H, 4.72; N, 6.91. Found: C, 62.06; H, 4.85; N, 6.52.

Crystal Structure Determination. *X-Ray Data Collection, Structure Solution, and Refinement.* Suitable crystals for the X-ray analysis of **3**, **4**, **6**, and **8** were obtained as described below. The crystals were placed in oil, and a single crystal was selected, mounted on a glass fiber, and placed in a low-temperature N_2 stream. X-ray diffraction data collection was carried out at 173(2) K on a Nonius Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The crystal-detector distance was 36 mm. Crystallographic and experimental details for the structure are summarized in Table 2. The structure was solved by direct methods using the program SHELXS-97.[83] The refinement and all further calculations were carried out using SHELXL-97.[84] The H atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters, unless otherwise stated. CCDC 830133 (**3**), 803952 (**4**), 830134 (**6**·0.5(H_2O)), and 830135 (**8**·3(CH_2Cl_2)) contain the supplementary crystallographic data for this paper and can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_ request/cif

*Compound **3**.* Crystals suitable for X-ray diffraction were obtained as red blocks by slow diffusion of pentane into a saturated solution of **3** in CH_2Cl_2. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2.

*Compound **4**.* Crystals suitable for X-ray diffraction were obtained as red plates by slow diffusion of pentane into a solution of **4** in CH_2Cl_2. In **4**, the non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. The carbon atoms C28, C29, C32, and C33 were found disordered in multiple positions and were refined with constrained anisotropic displacements (SHELXL EADP). Two crystallographically independent molecules are linked by hydrogen bonds in the asymmetric unit.

*Compound **6**.* Single crystals of **6**·0.5(H_2O) suitable for X-ray diffraction were obtained as red prisms by slow diffusion of pentane into a solution of **6** in CH_2Cl_2. One of the butyl groups was found disordered in two positions with unequal occupancy factors. These atoms were refined with constrained thermal and geometrical parameters. A severe disorder involved the cocrystallized solvent. One molecule of water (per asymmetric unit) was found not disordered, and its H atoms could be located. These were refined with constrained thermal and geometrical parameters. A number of electron density peaks, none higher than 3 e/Å^3, could not be assigned. Instead, a PLATON SQUEEZE procedure was applied,[85] resulting in improved quality for the main residue model. The calculation estimated a missing electron density of 534*e* over 950 Å^3 that can be assigned to a mixture of dichloromethane and pentane. Two crystallographically independent molecules are linked by hydrogen bonds in the asymmetric unit.

*Compound **8**.* Single crystals of **8**·3(CH_2Cl_2) suitable for X-ray diffraction were obtained as red blocks by slow diffusion of pentane into a solution of **8** in CH_2Cl_2. Residual electron density was found in the electron map, but any attempt to locate these atoms failed. Instead, a PLATON SQUEEZE procedure was applied.[85] The calculation estimated a missing electron density of 183*e*, consistent with four molecules of pentane (168*e*, 360 Å^3). This procedure resulted in an improved model for the main residue. Two of three dichloromethane molecules and the butyl chains (C7−C10 and C11−C14) and a phenyl group (C57−C62) were found disordered. One butyl group was refined on two positions having the α carbon atom in common and was refined with constrained thermal and geometric parameters, while any attempt to define the disorder of the phenyl and the second butyl failed. Instead, these atoms were refined with restrained thermal and geometric parameters.

■ ASSOCIATED CONTENT

Supporting Information. CIF file giving crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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