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Facile and Reversible 1,3-Dipolar Cycloaddition of Aryl Ketonitrones to Platinum(II)-Bound Nitriles: Synthetic, Structural, and Theoretical Studies

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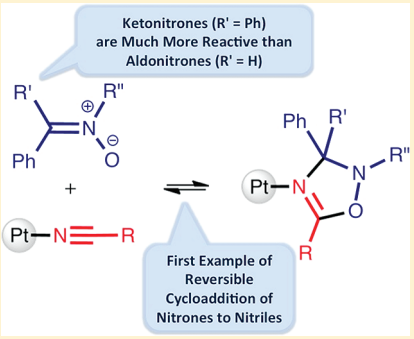
Supporting Information

ABSTRACT: The reaction between *trans*-$[PtCl_2(NCR)_2]$ (R = Et **1**, NMe_2 **2**, NEt_2 **3**, NC_5H_{10} **4**) and the acyclic triaryl ketonitrones $Ph_2C{=}N(O)C_6H_4R'$-*p* (R′ = H **5**, Me **6**, Cl **7**, OMe **8**) proceeds as a facile and consecutive two-step intermolecular cycloaddition to give the mono-cycloaddition products *trans*-$[PtCl_2(NCR)\{N^a{=}C(R)ON(C_6H_4R'\text{-}p)C^bPh_2\}]^{(a-b)}$ (R/R′ = Et/H **9**, Et/Me **10**, Et/Cl **11**, Et/OMe **12**, NMe_2/H **13**, NMe_2/Me **14**, NMe_2/Cl **15**, NMe_2/OMe **16**, NEt_2/H **17**, NEt_2/Me **18**, NEt_2/Cl **19**, NEt_2/OMe **20**, NC_5H_{10}/H **21**, NC_5H_{10}/Me **22**, NC_5H_{10}/Cl **23**, NC_5H_{10}/OMe **24**) and then the bis-2,3-dihydro-1,2,4-oxadiazole complexes *trans*-$[PtCl_2\{N^a{=}C(R)ON(C_6H_4R'\text{-}p)C^bPh_2\}_2]^{(a-b)}$ (R/R′ = Et/H **25**, Et/Me **26**, Et/Cl **27**, Et/OMe **28**, NMe_2/H **29**, NMe_2/Me **30**, NMe_2/Cl **31**, NMe_2/OMe **32**, NEt_2/H **33**, NEt_2/Me **34**, NEt_2/Cl **35**, NEt_2/OMe **36**, NC_5H_{10}/H **37**, NC_5H_{10}/Me **38**, NC_5H_{10}/Cl **39**, NC_5H_{10}/OMe **40**). The ketonitrones $Ph_2C{=}N(O)C_6H_4R'$-*p* were found to be unexpectedly much more reactive toward the platinum(II)-bound nitriles than the related aldonitrones *p*-$R'''C_6H_4CH{=}N(O)R''$ (R″ = Me, Ph; R‴ = H, Me), and the difference in the reactivity in 1,3-dipolar cycloaddition (DCA) of the keto- and aldonitrones was interpreted by theoretical calculations and was explained in terms of the orbital arguments as a result of the increase of the $HOMO_{nitrone}$ energy from aldo- to ketonitrones. The first example of the reversibility in metal-mediated DCA of nitrones to nitriles was observed, and this phenomenon, as follows from the performed theoretical study, is justified by the thermodynamic instability of the Pt^{II}-bound 3,3-diaryl-2,3-dihydro-1,2,4-oxadiazoles. Metal-free C^5-diphenyl-2,3-dihydro-1,2,4-oxadiazoles **42** and **43** were liberated from corresponding $(oxadiazole)_2Pt^{II}$ complexes **26** and **30** by treatment with excess NaCN, and these heterocycles were characterized by high-resolution ESI^+-MS and ^1H and $^{13}C\{^1H\}$ NMR spectroscopies.



INTRODUCTION

Metal-mediated cycloaddition (CA) of various dipoles to nitriles represents an efficient route to those free and/or coordinated heterocycles that could be either difficult to obtain or even inaccessible via metal-free protocols.[1−5] In particular, nitriles bound to platinum(IV) centers react with allyl anion dipoles, such as the acyclic nitrones R″R′C=N(O)R, under mild conditions, and this reaction has a general character that is applicable to a wide range of reactants and their various combinations.[1,6−12] In the past decade, a number of experimental and theoretical works were devoted to the 1,3-dipolar cycloaddition (DCA) of nitrones to nitriles,[6−16] and they were summarized in a recent review written by us.[1]

In terms of orbital interactions, the nitrone−nitrile DCAs are controlled predominantly by the interaction between the HOMO of a dipole and the LUMO of a dipolarophile.[17] Such reactions can be promoted (or inhibited) by using dipoles with electron-donor (or electron-acceptor in the case of the inhibition) substituents, and this statement is so far well supported by the experimental data.[9,10] Therefore, the general considerations suggest that the aldonitrones Ar(H)C=N(O)R bearing one acceptor aryl at the C atom should be more reactive toward RCN dipolarophiles than the *C*-diaryl ketonitrones $Ar_2C{=}N(O)R$, and in particular, Ph(H)C=N(O)Me is expected to exhibit the higher reactivity in DCA as compared to $Ph_2C{=}N(O)Ph$.

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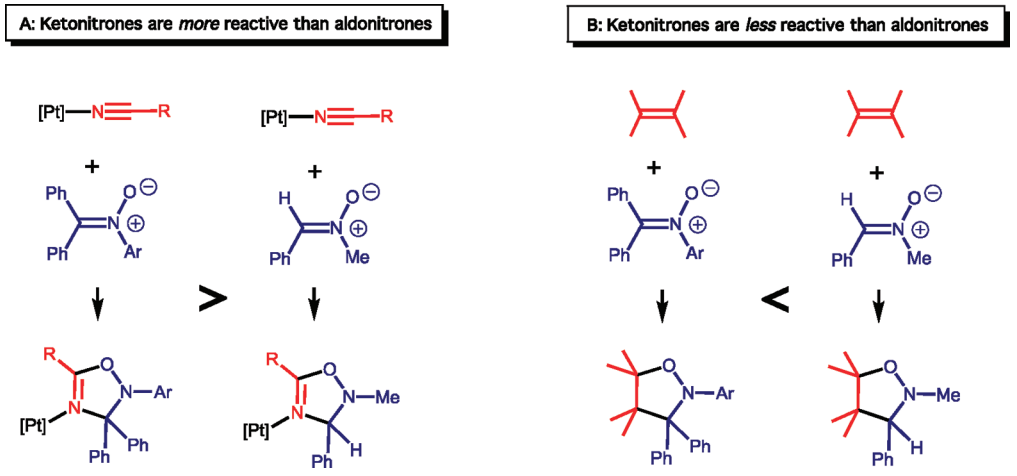
Scheme 1. Different Reactivities of Nitrones toward Nitrile Ligands and Alkenes



Taking all these in mind, we still attempted the reaction between the ketonitrone $Ph_2C{=}N(O)Ph$ and RCN ligands at a Pt^{II} center and observed unexpectedly high reactivity of this dipole in DCA. Indeed, it appeared to be much higher than the reactivity of the aldonitrone $Ph(H)C{=}N(O)Me$ (Scheme 1-A) and comparable only with one of the most reactive nitrones known, viz., 5,5-dimethylpyrroline *N*-oxide $\overline{CMe_2CH_2CH_2CH{=}N(O)}$.

One should also notice that although DCA of aldonitrones to nitrile ligands was repeatedly studied,[6,7,11] no single example for CA of ketonitrones to *nitrile* species was published to date. However, DCA of *N*-aryl ketonitrones to *alkenes* is known, and the reported data[18] indicate a much lesser reactivity of *N*-aryl ketonitrones as compared to *N*-aryl aldonitrones (Scheme 1-B).

All these observations, along with the literature data, prompted us to study systematically CA of the ketonitrones $Ph_2C{=}N(O)Ar$ to nitrile species at platinum(II) centers. Our goals were at least fourfold: (i) to study DCA of *N*-aryl ketonitrones to metal-bound nitrile species and to attempt this CA with uncomplexed nitriles to verify the effect of the metal center on the reaction; (ii) to compare the reactivity of *N*-aryl ketonitrones and *N*-aryl aldonitrones in DCA to nitrile ligands at both experimental and theoretical levels; (iii) to provide theoretical interpretation for the opposite orders of reactivity of aldo- and ketonitrones in CA to alkenes or nitriles (Scheme 1); (iv) to characterize complexes bearing 2-aryl-3,3-diphenyl-2,3-dihydro-1,2,4-oxadiazoles and to develop a route for the liberation of these yet unknown heterocyclic species from their Pt^{II} complexes.

RESULTS AND DISCUSSION

For the current work, the nitrile complexes *trans*-$[PtCl_2(NCR)_2]$ (R = Et **1**, NMe_2 **2**, NEt_2 **3**, NC_5H_{10} **4**) and the *N*-aryl ketonitrones $Ph_2C{=}N(O)C_6H_4R'$-*p* (R′ = H **5**, Me **6**, Cl **7**, OMe **8**) were addressed as reactants (Scheme 2). Synthesis and characterization of new nitrones **6**–**8** are given in the Supporting Information.

The reaction between each of **1**–**4** and each of **5**–**7** (in all possible combinations; the reactions of **8** see later) in a molar ratio of 1:1 in $CHCl_3$ at room temperature is complete in 5 h, giving mono-cycloadducts (mono-CAs) **9**–**11**, **13**–**15**, **17**–**19**, and **21**–**23** (NMR yields ca. 100%; isolated yields ca. 80% after column chromatography on SiO_2) (Scheme 2, route A). All these species are derived from DCA of the nitrones to one nitrile ligand of the Pt^{II} complexes.

Scheme 2. Studied Cycloadditions

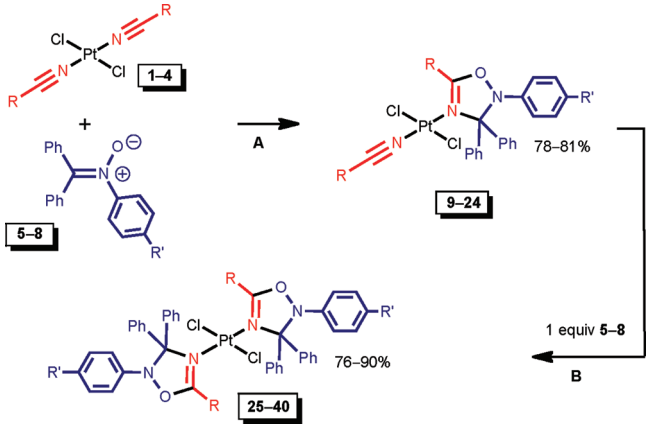


Table 1. Compound Numbering in Scheme 1

R		R′ = H	R′ = Me	R′ = Cl	R′ = OMe
		5	6	7	8
Et	1	9/25	10/26	11/27	12/28
NMe_2	2	13/29	14/30	15/31	16/32
NEt_2	3	17/33	18/34	19/35	20/36
NC_5H_{10}	4	21/37	22/38	23/39	24/40

All reactions of **1**–**4** with 2 equiv of **5**–**7** proceed as a consecutive DCA and lead to bis-cycloadducts (bis-CAs) **25**–**27**, **29**–**31**, **33**–**35**, and **37**–**39** (Scheme 2). The syntheses of these bis-CAs were performed by three routes, depending on solubility of the products, viz., (i) in $CHCl_3$ solution in a 1:2 molar ratio of the nitrile complex (**1** or **2**) and the nitrone (each of **5**–**7**) accompanied by precipitation of **25**–**27** and **29**–**31**; (ii) in THF solution in a 1:2 molar ratio between the nitrile complex (**3** or **4**) and the nitrone (**6** or **7**) accompanied by precipitation of **34**, **35**, **38**, and **39**; (iii) in $CHCl_3$ solution in a 1:14 molar ratio between the nitrile complex (**3** or **4**) and the nitrone (**5**) followed by separation of **33** or **37** by column chromatography. A detailed description of these procedures is given in the paragraphs that follow.

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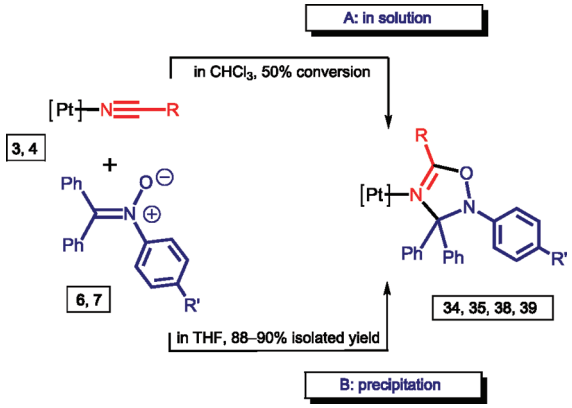
Synthetic Approach (i). The reaction of **1** or **2** with each of **5**–**7** (2 equiv) at 35 °C in a chloroform solution proceeds selectively, resulting in precipitation of bis-CA species **25**–**27** and **29**–**31**. TLC monitoring of the reaction mixtures demonstrates that the conversion of the starting complexes into corresponding mono-CAs **9**–**11** and **13**–**15** (route A) proceeds for ca. 2 h, whereas the total conversion into bis-CAs **25**–**27** and **29**–**31** (route B) takes ca. 5 h (isolated yields achieved by this synthetic approach are 89–90%).

The reaction of **3** or **4** with each of **5**–**7** (2 equiv) in a chloroform solution at 35 °C gave **33**–**35** and **37**–**39** (as confirmed by high-resolution ESI-MS and ^{1}H NMR), but DCA was not accompanied by their precipitation. The conversion of **3** or **4** into corresponding mono-CA species **17**–**19** or **21**–**23** proceeds for ca. 2.0–2.5 h, while only 50% conversion (based on NMR monitoring) into bis-CAs **33**–**35** and **37**–**39** occurs in 5 h (Scheme 3, A). The complete conversion of mono-CAs **17**–**19** and **21**–**23** to bis-CAs **33**–**35** and **37**–**39** under these conditions was not achieved even after 2 d, and gradual degradation of mono-CA species to give a broad mixture of yet unidentified products (7 spots on TLC) was observed.

Scheme 3. Solvent Dependence of DCA That Is Performed at 35 °C for 5 h



Synthetic Approach (ii). The change of the solvent from $CHCl_3$ to THF in the reaction of **3** or **4** with 2 equiv of **6** or **7** (in all combinations) led to precipitation of **34**, **35**, **38**, and **39**, respectively, furnishing bis-CAs for 5 h at 35 °C (Scheme 3, B). After 5 h, corresponding mono-CA species were not detected in the reaction mixture by both TLC and ESI-MS methods.

The treatment of **3** or **4** with 2 equiv of **5** at 35 °C in THF for 5 h led to the generation of **33** or **37** (as confirmed by TLC and ESI-MS), but the reaction was not accompanied by their precipitation and the conversion of **3** (or **4**) into **33** (or **37**) was not complete.

Synthetic Approach (iii). The complete conversion of **3** (or **4**) into **33** (or **37**) was achieved in a $CHCl_3$ solution by the use of a 7-fold excess (14 equiv) of the corresponding nitrone for 6 h at 35 °C. Complexes **33** and **37** were isolated by column chromatography on SiO_2 in 76–79% yields.

Nitrone **8**, which is the most reactive from the studied series, reacts with **1**–**4** in a molar ratio of 1:1 at 20–25 °C to give, after 2–3 min, a broad mixture of products (8 spots on TLC). However, decreasing the temperature to −15 °C reduces the reaction rate and improves the selectivity to accomplish good yields of pure mono-CA complexes **12**, **16**, **20**, and **24** after 2 d (NMR yields ca. 100%, isolated yields ca. 80% after column chromatography on SiO_2). Because of the high reactivity of **8**, interaction of this 1,3-dipole with each of **1**–**4** (molar ratio 2:1) proceeds with low degree of selectivity at 20–25 °C, and this method for generation of bis-CAs could not be recommended as preparative. Bis-CA products **28**, **32**, **36**, and **40** were obtained by treatment of each of **1**–**4** with 14 equiv of **8** at −15 °C. After 3–4 h, when the conversion of the starting complexes into corresponding mono-CAs was completed, the reaction mixture was heated to 35 °C and then stirred for 5 h to give **28**, **32**, **36**, and **40** in 78–80% isolated yields after column chromatography.

Thus, in contrast to previous studies,[6] we found that ketonitrones **5**–**8** undergo facile DCA to Pt^{II}-bond alkylnitriles (R = Et) and dialkylcyanamides (R = NMe_2, NEt_2, NC_5H_{10}). Surprisingly, the reactivity of the ketonitrones $Ph_2C{=}N(O)Ar$ is sufficient to react even with the nitrile ligand bearing the electron-donor Et substituent. Earlier works[6,7,16,19–22] give evidence of a lower reactivity of *N*-alkyl aldonitrones toward DCA to RCN ligands in comparison with **5**–**8**. Thus, *Z*-ArCH=N(O)Alk does not react with the alkylcyanide ligand EtCN in their Pt^{II} complexes and gives the cycloadducts only when they are strongly activated by a Pt^{IV} center or in Pt^{II} complexes bearing more dipolarophilic dialkylcyanamide ligands.[11]

In this context, the attention should be drawn to the opposite reactivity modes of the acyclic aldo- and ketonitrones in DCA to the C=C bond,[18] where the reactivity of the nitrones in the reaction with alkylidenecyclopropanes decreases along the series *C*-aryl, *N*-alkyl aldonitrones > *C*,*C*-diphenyl, *N*-aryl ketonitrones (Scheme 1-B). The observed difference in the reactivity modes of nitrile ligands (this work; Scheme 1-A) and methylenecyclopropanes (Scheme 1-B) toward DCA was rationalized in the Theoretical Studies section (see later) and also partially presented in the Supporting Information.

Reversibility of DCA. In the previous section, we indicated that the completeness of the conversion of mono-CAs to corresponding bis-CA species depends on the nature of the employed solvent that determines the solubility of bis-CA products. Thus, the reaction given in route B (Scheme 3) occurs faster and with a higher degree of conversion in those solvents, where bis-CAs precipitate from the reaction mixtures. These experimental observations give collateral evidence favoring the reversibility of DCA. However, NMR monitoring of **27**, taken as an example, in $CDCl_3$ (10 d, 20–25 °C) did not reveal the generation of products originating from retro-DCA, and these data indicate that if the equilibrium exists, it is so strongly shifted to bis-CAs that the quantity of retro-CA species is below ^{1}H NMR threshold values.

To obtain data additionally supporting the reversibility, we performed the following experiments. First (Scheme 4), a suspension of **27** was treated with 10 equiv of **6** in $CHCl_3$ at 20–25 °C upon continuous stirring. After 120 h, **7**, **41**, and **26** were detected (by TLC and ESI-MS) in the reactions mixture along with the starting materials (**27** and **6**). Complex **41** was isolated by column chromatography on SiO_2 in ca. 8% yield, and it was characterized by NMR and high-resolution ESI-MS (see Experimental Section). Second (Scheme 5), a suspension of **27** was stirred at 20–25 °C with 10 equiv of **2** in $CHCl_3$. After 120 h, **11** and **15** were isolated from the reaction mixture and separated by column chromatography along with unreacted **27** and **2**.

We also conducted a blank experiment indicating that the reversibility of DCA is specific for metal-bound species. Prolonged (120 h) stirring of nitrone **6** or the nitrile $NCNMe_2$ with free 5-ethyl-3,3-diphenyl-2-(*p*-tolyl)-2,3-dihydro[1,2,4]oxadiazole

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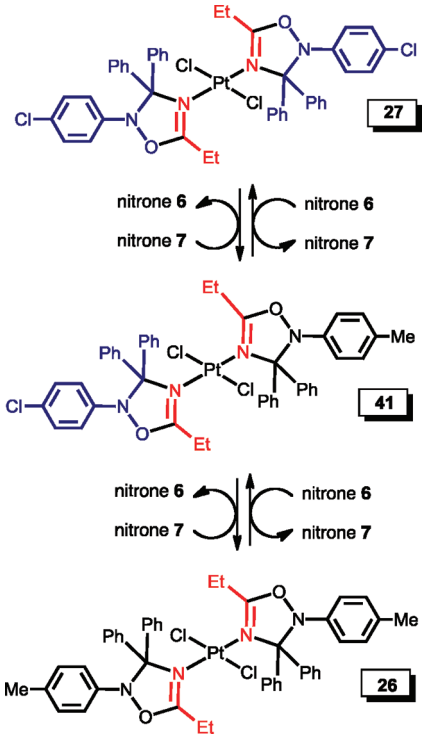
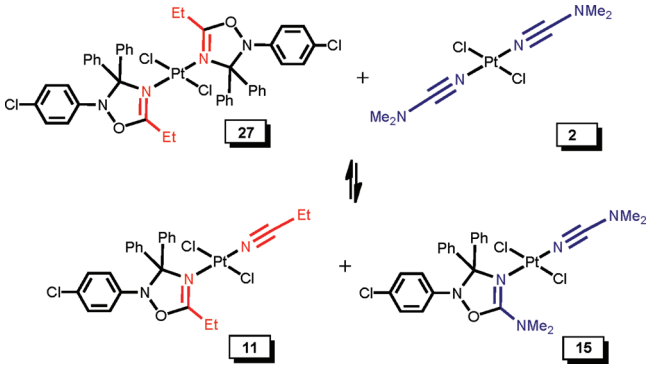
Scheme 4. Nitrone Exchange in 27



Scheme 5. Exchange between 27 and 2

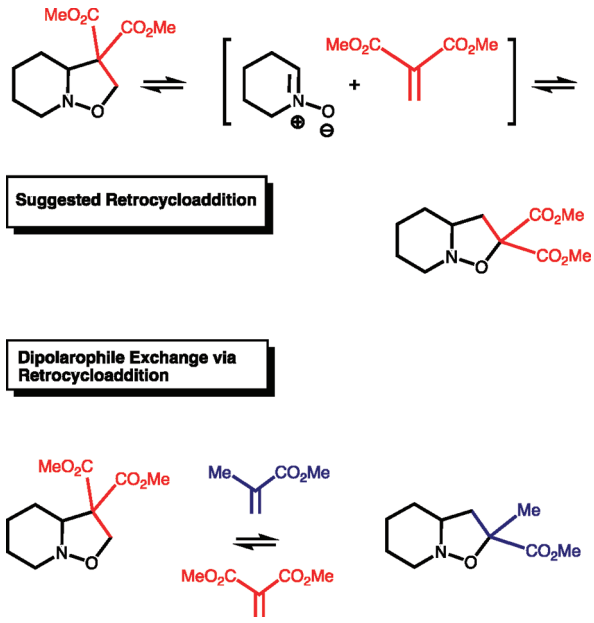


(**42**) (or 5-(dimethylamino)-3,3-diphenyl-2-(*p*-tolyl)-2,3-dihydro[1,2,4]oxadoazole, **43**) (see below) at 35 °C gave no evidence for the appearance of other heterocycles in the mixture, and **6** or the nitrile $NCNMe_2$ and **42** (or **43**) remain intact.

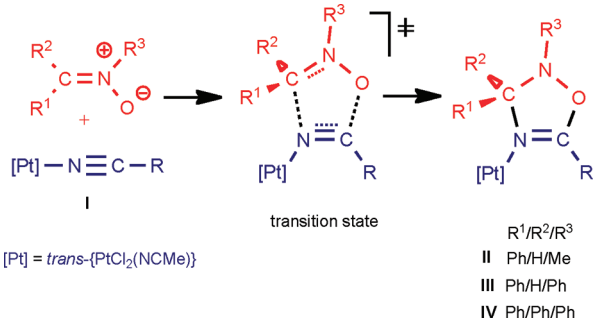
To the best of our knowledge we found the first example of reversibility in metal-mediated DCA of *nitrones to nitriles*, although one example favoring the reversibility of DCA of *nitrones to alkenes* is known in metal-free organic chemistry; that is, the alkene−nitrone cycloadduct (Scheme 6) undergoes isomerization (via retrocycloaddition) or dipolarophile exchange with an excess of another alkene.[23,24]

Theoretical Studies. In order to interpret the experimentally found substituent-dependent chemical behavior of various nitrones toward DCA to nitriles, quantum-chemical calculations of DCA of two aldonitrones in the *Z*-form, i.e., PhCH═N(O)Me and PhCH═N(O)Ph, and one ketonitrone, Ph_2C═N(O)Ph, with acetonitrile—free and coordinated to the Pt^{II} center in the complex *trans*-$[PtCl_2(NCMe)_2]$ (**I**) (Scheme 7)—have been carried

Scheme 6. Isomerization (via retrocycloaddition) or Dipolarophile Exchange with Excess of Another Alkene



Scheme 7. Reaction of the Nitrones with *trans*-$[PtCl_2(NCMe)_2]$



out at the B3LYP level of theory. The calculations indicate that, first, DCAs of all nitrones to free MeCN belong to the neutral type II of the Sustmann classification (i.e., controlled by both $HOMO_{dipole}/LUMO_{dipolarophile}$ and $LUMO_{dipole}/HOMO_{dipolarophile}$ interacions; the reactions controlled predominantly by the $HOMO_{dipole}/LUMO_{dipolarophile}$ or $HOMO_{dipolarophile}/LUMO_{dipole}$ interactions belong to type I or type III, respectively).[17,26] The $HOMO_{nitrone}$–$LUMO_{nitrile}$ gap is only 0.74−1.12 eV smaller than the $HOMO_{nitrile}$–$LUMO_{nitrone}$ gap (Figure 1-A). The coordination of MeCN to Pt^{II} in complex **I** leads to an energy decrease of both $\pi_{\perp}$(CN) and $\pi^*_{\perp}$(CN) MOs of the nitrile. As a result, the reactions with complex **I** are clearly of type I with the predominant $HOMO_{nitrone}$–$LUMO_{nitrile}$ type of orbital interaction (Figure 1-B). The lowering of the $LUMO_{nitrile}$ energy on going from MeCN to **I** explains the activation of nitriles upon coordination.[9,26−30] In the studied nitrone series, the $HOMO_{nitrone}$ energy slightly increases (the $HOMO_{nitrone}$–$LUMO_{nitrile}$ gap decreases) along the row PhCH═N(O)Me ≤ PhCH═N(O)Ph < Ph_2C═N(O)Ph. Thus, the simple qualitative consideration of molecular orbitals suggests that the reactivity of nitrones should increase along the same sequence.

Second, the mechanism of DCAs to free MeCN is concerted, highly synchronous and includes the formation of a five-membered

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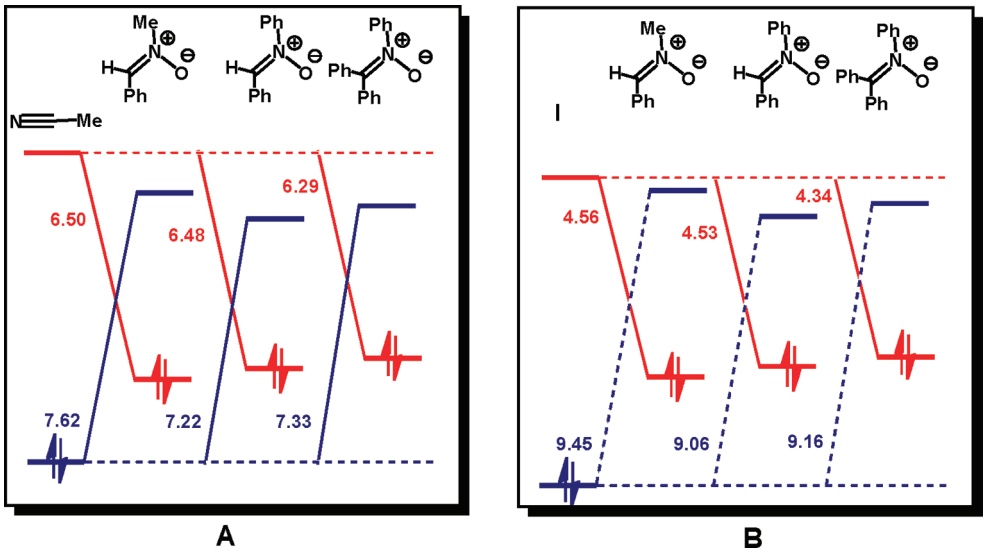

Figure 1. Relative energies (in eV) of the frontier MOs of nitrones and nitriles.

cyclic transition state. The synchronicity parameter, S_y, is 0.90, 0.92, and 0.87 for the reactions of PhCH=N(O)Me, PhCH=N(O)Ph, and Ph_2C=N(O)Ph, respectively (S_y is 1 for perfectly synchronous cycloadditions and 0 for the stepwise mechanism; see Computational Details in the Experimental Section). In contrast, the mechanism of the reactions with **I** is asynchronous with S_y values of 0.67, 0.69, and 0.56 for the nitrones indicated above, correspondingly.

Third, the coordination of MeCN results in a dramatic decrease of the activation energies from 31.7−34.1 kcal/mol (for DCAs to MeCN) to 22.5−25.9 kcal/mol (for DCAs to **I**) (Table 2). Both aldonitrones PhCH=N(O)Me and PhCH=N(O)Ph exhibit similar reactivity. In contrast, the ketonitrone Ph_2C=N(O)Ph is more reactive than the aldonitrones by 1.5−2.4 kcal/mol (reaction with MeCN) and 2.9−3.4 kcal/mol (reaction with **I**), i.e., by a factor of 13 to 310, which is in agreement with the qualitative experimental observations described above. The calculated activation barriers (gas-phase activation energies) correlate well with the $HOMO_{nitrone}$ energies (Table 2, Figure 1). Thus, the higher reactivity of the ketonitrone versus the aldonitrones can be interpreted in terms of the orbital arguments as a result of the higher HOMO energy of Ph_2C=N(O)Ph compared to PhCH=N(O)Me and PhCH=N(O)Ph.

Table 2. Calculated Activation and Reaction Energies (in kcal/mol) for DCAs of Nitrones to Nitriles in Gas-Phase and CH_2Cl_2 Solution (in parentheses)

dipolarophile	nitrone	E_a	$\Delta G^{\ddagger}$	ΔE	ΔG
NCMe	Ph_2C=N(O)Ph	20.8	30.5	−9.0	−0.2
		(26.0)	(31.7)	(−3.1)	(+1.7)
	PhCH=N(O)Ph	23.0	32.5	−9.6	−1.0
		(27.6)	(33.2)	(−4.4)	(+0.4)
	PhCH=N(O)Me	24.7	33.9	−7.4	+0.7
		(28.7)	(34.1)	(−2.7)	(+1.4)
I	Ph_2C=N(O)Ph	6.2	16.8	−10.6	+1.4
		(16.1)	(22.5)	(+0.1)	(+7.4)
	PhCH=N(O)Ph	11.5	22.6	−18.0	−7.8
		(19.2)	(25.9)	(−8.0)	(−2.1)
	PhCH=N(O)Me	11.7	21.9	−17.4	−7.8
		(19.6)	(25.4)	(−7.9)	(−2.6)

Fourth, the reactions with free MeCN are only slightly endoergonic, the ΔG_s values being similar for all three nitrones (0.4−1.7 kcal/mol, Table 2). In contrast, DCA of the ketonitrone Ph_2C=N(O)Ph to the Pt complex **I** is clearly less thermodynamically favorable than the reactions of the aldonitrones PhCH=N(O)Ph and PhCH=N(O)Me. These results are in agreement with our experimental observations on the reversibility of DCA of the ketonitrones (but not aldonitrones) to the nitriles in the $(RCN)Pt^{II}$ complexes. The different thermodynamic behavior of the keto- and aldonitrones toward the complexed nitriles is conceivably accounted for by a destabilization of product **IV** due to the steric repulsion between the phenyl groups and the metal fragment. Indeed, an introduction of the second Ph group at the C atom of the C=N bond of a nitrone results in significant conformational changes of the Ph groups and of the metal fragment relative to the oxadiazole ring (Figure 2). The PtN(1)C(2) angle in **IV** is clearly smaller than

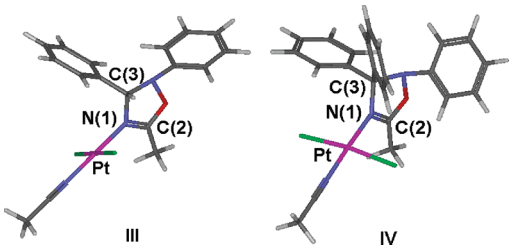

Figure 2. Equilibrium geometries of **III** and **IV**.

that in **III** (120° and 128°, respectively). The N(1)C(3) bond lengths are 1.524 and 1.480 Å for **IV** and **III**, correspondingly. All this indicates noticeable steric strain in the molecule of **IV**.

For comparison with CAs to nitriles, the reactions of the same three nitrones with methylenecyclopropane, CH_2=$C^aCH_2C^bH_2^{(a-b)}$, have also been calculated. They also belong to type II; both $HOMO_{nitrone}$−$LUMO_{alkene}$ and $HOMO_{alkene}$−$LUMO_{nitrone}$ gaps are somewhat larger for the reaction with PhCH=N(O)Me, indicating that in terms of the frontier MO theory this nitrone should be the least reactive with methylenecyclopropane. Indeed, the gas-phase activation energy, E_a, increases along the series of the dipoles PhCH=N(O)Ph (20.1 kcal/mol) < Ph_2C=N(O)Ph

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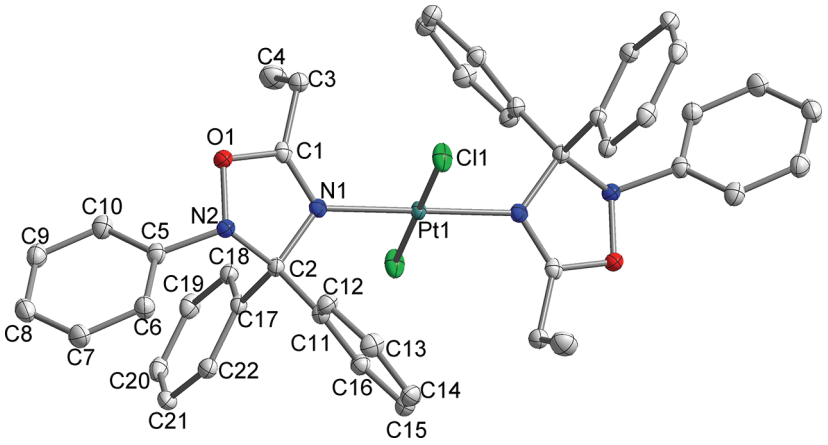

Figure 3. View of **25** with the atomic numbering scheme. Thermal ellipsoids are given at the 50% probability level. Hydrogen atoms are omitted for clarity.

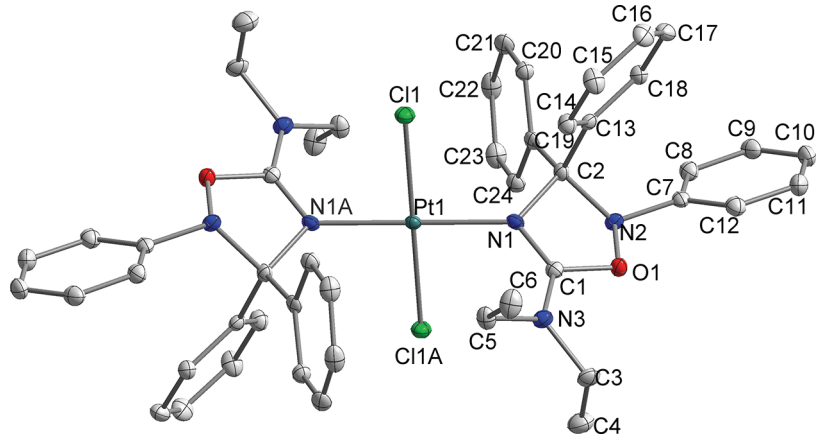

Figure 4. View of **33** with the atomic numbering scheme. Thermal ellipsoids are given at the 50% probability level. Hydrogen atoms are omitted for clarity.

(21.7 kcal/mol) < PhCH═N(O)Me (22.1 kcal/mol) (Table S2 in Supporting Information). However, in terms of Gibbs free energy of activation in CH_2Cl_2 solution, $\Delta G_s^{\ddagger}$, the ketonitrone Ph_2C═N(O)Ph becomes less reactive than PhCH═N(O)Me, by 1.5 kcal/mol, indicating the importance of the entropic contribution and solvent effects in these processes. Note that the difference of the $\Delta G_s^{\ddagger}$ values, 1.5 kcal/mol, corresponds to the ratio of the reaction rates, ca. 13, and, therefore, can explain the experimentally observed lower reactivity of ketonitrones toward alkylidenecyclopropanes compared to aldonitrones.[18] Some additional discussion of these processes is given in the Supporting Information.

Characterization of 9–40. Complexes **9–40** were obtained as yellow solids and characterized by elemental analyses (C, H, N), high-resolution ESI^+-MS, IR, and ^1H and $^{13}C\{^1H\}$ NMR spectroscopies and also by X-ray diffraction (for **25** and **33**). All platinum species gave satisfactory microanalyses. In the ESI^+-MS, the typical ions that were detected are $[M + H]^+$, $[M + Na]^+$, and $[M + K]^+$. A comparison of the IR spectra of the products with those of the starting *trans*-$[PtCl_2(RCN)_2]$ indicated the absence of ν(C≡N) stretching vibrations at ca. 2300 cm^{-1} for **25–40**, while for **9–24** these stretches are displayed in the region from 2287 to 2305 cm^{-1}. The presence of intensive ν(C═N) vibrations in the range between 1636 and 1667 cm^{-1} was detected in the IR spectra of all complexes.

For **9–40**, signal integration in the ^1H NMR spectra gives evidence that the reaction between each of the coordinated nitriles and the nitrone proceeds in a 1:1 ratio. Both ^1H and $^{13}C\{^1H\}$ NMR spectra of **9–24** exhibit signals from the oxadiazole and the nitrile ligands. The ^1H NMR spectra of **13–24** display broad (owing to the hindered rotation around the C^5–NR_2 bond) singlets of the CH_3 protons from C^5–NMe_2 (**13–16**; 3.75–3.82 ppm), the CH_2 protons from C^5–NEt_2 (**17–20**; 4.36–4.38 ppm), and the α-CH_2 protons from C^5–C_5H_{10} (**21–24**; 4.38 ppm). The less broad signals from these protons for bis-CA species are low-field shifted by 0.70–0.80 ppm relative to the corresponding signals from mono-CAs. The quartets due to the CH_2 protons from C^5–Et in the NMR spectra of **9–12** and **25–28** appeared in the same range for both mono- and bis-CA species (2.93 for **9** and **25**; 2.81 for **10** and **26**, **12** and **28**; 2.82 for **11** and **27**). In the $^{13}C\{^1H\}$ NMR spectra, the peaks due to C^5═N (159.6–161.4) and C^3 (98.0–98.5 ppm) were recognized.

Complexes **25** and **33** were characterized by a single-crystal X-ray diffraction. Thus, in **25** and **33**, the coordination polyhedra of the Pt atoms are slightly distorted square planes with the hetetocyclic ligands in the *trans*-position. The Pt(1)–N(1) (2.026(2) Å for **25** and 2.037(2) Å for **33**; Table 3) bonds lengths are typical for (imine)Pt^{II} species,[31] while the Pt–Cl bonds are specific for platinum(II) chloride species.[31] The N(1)–C(1) distances (1.282(3) Å for **25** and 1.311(3) Å for

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Table 3. Selected Bond Lengths (Å) and Angles (deg) in 25 and 33

	25	33
Pt(1)−N(1)	2.026(2)	2.037(2)
Pt(1)−Cl(1)	2.3010(5)	2.3053(6)
O(1)−C(1)	1.336(3)	1.356(3)
O(1)−N(2)	1.473(2)	1.462(3)
N(1)−C(1)	1.282(3)	1.311(3)
N(1)−C(2)	1.492(3)	1.496(3)
N(2)−C(2)	1.519(3)	1.519(3)
N(1A)[a]−Pt(1)−N(1)	180.0	180.0
Cl(1A)[a]−Pt(1)−Cl(1)	180.0	180.0
N(1A)[a]−Pt(1)−Cl(1)	93.36(5)	87.85(6)
N(1)−Pt(1)−Cl(1)	86.64(5)	92.15(6)
C(1)−O(1)−N(2)	104.9(2)	103.1(2)
C(1)−N(1)−C(2)	108.7(2)	105.7(2)
C(1)−N(1)−Pt(1)	123.9(2)	127.8(2)
C(2)−N(1)−Pt(1)	126.8(1)	125.5(2)
O(1)−N(2)−C(2)	103.3(2)	101.2(2)
N(1)−C(1)−O(1)	115.5(2)	114.4(2)
N(1)−C(2)−N(2)	99.8(2)	97.6(2)

[a]Symmetry transformations used to generate equivalent atoms: $-x, -y, -z$ for **25** and $-x+1, -y+1, -z$ for **33**.

33) are characteristic for the N=C double bond,[31] while the N(1)−C(2) and N(2)−C(2) in **25** and **33** (1.492(3) and 1.519(3) Å for **25** and 1.496(3) and 1.519(3) Å for **33**) are specific for the N−C single bonds.[31]

*Liberation of 2,3-Dihydro-1,2,4-oxadiazoles from **26** and **30**.* Several methods for liberation of the strongly bound imines and nitrogen heterocycles from their Pt^{II} complexes have been developed, and they are based on displacement with an excess of diphosphine,[32−36] monodentate and bidentate amines bearing two sp^3-*N* donor centers,[10,21,37] or alkali metal cyanides.[11] The latter method (initially suggested by Leung and colleagues[38] for liberation of some chelated phosphine ligands strongly bound to Pt^{II} center) could be applied, due to its high efficiency, for decoordination of 2,3-dihydro-1,2,4-oxadiazole ligands bearing a strong electron-donor substituent at C^{5a} atom and strongly bound to a Pt^{II} center.[11]

To illustrate the methodology of the liberation and to open up a route to C^3-diphenyl-2,3-dihydro-1,2,4-oxadiazoles, we addressed two complexes (**26** and **30**) derived from different nitriles bearing alkyl and dialkylamino substituents, respectively. Accordingly, we observed that treatment of **26** and **30** with NaCN (8 equiv, 35 °C, 3 d) leads to almost quantitative formation of the free 5-ethyl-3,3-diphenyl-2-(*p*-tolyl)-2,3-dihydro[1,2,4]oxadiazole (**42**) and 5-(dimethylamino)-3,3-diphenyl-2-(*p*-tolyl)-2,3-dihydro[1,2,4]oxadiazole (**43**) (Scheme 8). These metal-free species were characterized by high-resolution ESI^+ mass spectrometry and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. In the ESI^+-MS, the observed peaks were attributed to the ions $[M + Na]^+$. $^{13}C\{^1H\}$ NMR spectra of the 2,3-dihydro-1,2,4-oxadiazoles demonstrate all signals specific for these heterocycles; the liberated species exhibit signals from C^{3a} (96.3−97.5 ppm) and C=N (161.2−162.0 ppm). The former signal is high field shifted (by ca. 1.0−1.5 ppm) and latter low field shifted (by 1−3 ppm) relative to the corresponding signals in (2,3-dihydro-1,2,4-oxadiazole)$_2Pt^{II}$ complexes **26** and **30**.

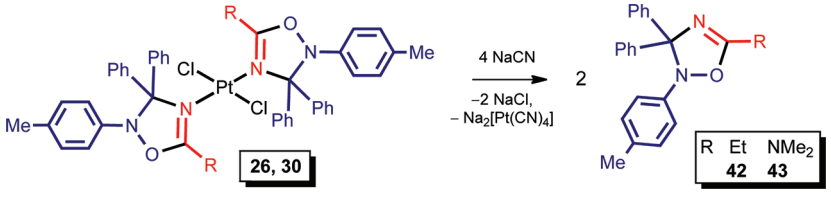
FINAL REMARKS

We found that the RCN (R = Alk, NR'_2) ligands in platinum(II) complexes **1**−**4** are involved in facile DCA with the acyclic ketonitrones, and the cycloaddition proceeds rapidly under mild conditions. This observation indicates that the ketonitrones are unexpectedly much more reactive toward metal-bound nitriles than the corresponding aldonitrones (e.g., in $[PtCl_2(EtCN)_2]$, the EtCN ligand easily reacts with **5**−**8** at 20−25 °C for 5 h, while the *N*-alkyl aldonitrones ArCH=N(O)R′ do not react[6] with this complex even under more drastic (50 °C, 30 d) conditions). The high reactivity of the ketonitrones is comparable only with one of the most reactive nitrones known, viz., 5,5-dimethylpyrroline *N*-oxide, $CMe_2CH_2CH_2CH{=}N(O)$, and this finding opens up a route for the generation of various 3,3-diaryl-2,3-dihydro-1,2,4-oxadiazoles starting even from such inactivated nitrile species as AlkCN.

The substantially different chemical behavior of the keto- and aldonitrones was interpreted by theoretical calculations. The higher reactivity of ketonitrones may be explained in terms of the orbital arguments as a result of the increase of the $HOMO_{nitrone}$ energy from aldo- to ketonitrones. Such an increase, in turn, is related to a different electronic effect imposed by the phenyl substituents in aldo- and ketonitrones. Indeed, in the former, the Ph group at the C atom is situated in the C=NO plane of the nitrone, it is involved in the conjugation, and acts as a conventional electron-acceptor substituent. In the ketonitrones, both Ph groups at the C atom are out of the C=NO plane due to steric repulsion (the dihedral angles are 25° and 58° for $Ph_2C{=}N(O)Ph$). Phenyls are not involved in the conjugation and, hence, act as electron-donor rather than electron-acceptor substituents, providing higher $HOMO_{nitrone}$ energy. In contrast to CA of ketonitrones to the RCN ligands, in the reaction with alkylidenecyclopropanes,[18] the ketonitrones are less reactive than the relevant aldonitrones. However, in this case, the main factors determining the relative reactivity of the dipoles are the entropic contribution and the solvation rather than the frontier MO energies (see the Supporting Information for details of our theretical study).

In this work, we also found the first example of the reversibility in metal-mediated DCA of *nitrones to nitriles*, and this unusual phenomenon was explained by the thermodynamic instability of Pt^{II}-coordinated 3,3-diaryl-2,3-dihydro-1,2,4-oxadiazoles. Theoretical calculations demonstrate that DCA products of the ketonitrones to the nitrile ligands are less thermodynamically stable than those derived from CA of the aldonitrones.

Scheme 8. Liberation of the 2,3-Dihydro-1,2,4-oxadiazoles



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The lower stability of DCA products of ketonitrones is accounted for by steric repulsions between the phenyl groups and the metal fragment. When decoordinated, 3,3-diaryl-2,3-dihydro-1,2,4-oxadiazoles exhibit sufficient stability due to the absence of the steric repulsion from the metal center.

EXPERIMENTAL SECTION

Materials and Instrumentation. Solvents were obtained from commercial sources and used as received. Complexes $[PtCl_2(RCN)_2]$ (R = Et, NMe_2, NEt_2, NC_5H_{10}) were synthesized in accord with the published procedures.[39,40] Nitrones **5**−**8** were obtained according to the previously described protocol[41] by the reaction of aryl nitroso compounds with diphenyl diazomethane in diethyl ether at room temperature (60−85%). Three of the four nitrones (viz., **6**−**8**) were not previously described, and their characterization is given in the Supporting Information. C, H, and N elemental analyses were carried out by the Department of Organic Chemistry of Saint-Petersburg State University on a Hewlett-Packard 185B carbon hydrogen nitrogen analyzer. Electrospray ionization mass spectra were obtained on a Bruker micrOTOF spectrometer equipped with an electrospray ionization (ESI) source. The instrument was operated in both positive and negative ion mode using a m/z range of 50−3000. The capillary voltage of the ion source was set at −4500 V (ESI^+-MS) and the capillary exit at ±(70−150) V. The nebulizer gas flow was 0.4 bar, and drying gas flow 4.0 L/min. For ESI species were dissolved in MeOH or MeCN, and $NaBF_4$ was used as additional ionization agent. In the isotopic pattern, the most intensive peak is reported. TLC was performed on Merck 60 F_{254} SiO_2 plates. Infrared spectra (4000−400 cm^{-1}) were recorded on a Shimadzu FTIR-8400S instrument in KBr pellets. ^1H and ^{13}C NMR spectra were measured in $CDCl_3$ on a Bruker DPX-300 spectrometer at ambient temperature.

X-ray Diffraction Study. Single-crystal X-ray diffraction experiments were carried out with a Bruker SMART APEX II diffractometer (graphite-monochromated Mo Kα_α radiation, λ = 0.71073 Å, ω-scan technique, T = 100(2) K). The APEX II software[42] was used for collecting frames of data, indexing reflections, determination of lattice constants, integration of intensities of reflections, and scaling and absorption correction, and SHELXTL[43] for space group and structure determination, refinements, graphics, and structure reporting. The structures were solved by direct methods and refined by the full-matrix least-squares technique against F^2 with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were placed geometrically and included in the structure factor calculation in the riding motion approximation. The principal experimental and crystallographic parameters are presented in Table S1 (Supporting Information).

Computational Details. The full geometry optimization of all structures and transition states has been carried out at the DFT/HF hybrid level of theory using Becke's three-parameter hybrid exchange functional in combination with the gradient-corrected correlation functional of Lee, Yang, and Parr (B3LYP)[44] with the help of the Gaussian-03[45] program package. No symmetry operations have been applied. The geometry optimization was carried out using a quasi-relativistic Stuttgart pseudopotential that described 60 core electrons and the appropriate contracted basis set (8s7p6d)/[6s5p3d][46] for the platinum atom and the 6-31G(d) basis set for other atoms. Then, single-point calculations were performed on the basis of the equilibrium geometries found using the 6-311+G(d,p) basis set for nonmetal atoms. Previously,[9,26,27] this level of theory was found as a reasonable one for the study of reactions of nitrones with nitriles and isocyanides. The basis set superposition error was not estimated because it weakly affects the activation and reaction energies of cycloadditions to nitriles, as it was shown previously.[28−30]

The Hessian matrix was calculated analytically for the optimized structures in order to prove the location of correct minima (no imaginary frequencies) or saddle points (only one negative frequency) and to estimate the thermodynamic parameters, the latter being calculated at 25 °C. The nature of all transition states was investigated by the analysis of vectors associated with the imaginary frequency.

Total energies corrected for solvent effects (E_s) were estimated at the single-point calculations on the basis of gas-phase geometries at the CPCM-B3LYP/6-311+G(d,p)//gas-B3LYP/6-31G(d) level of theory using the polarizable continuum model in the CPCM version,[47,48] with CH_2Cl_2 as solvent. The UAKS model was applied for the molecular cavity. The entropic term in CH_2Cl_2 solution (S_s) was calculated according to the procedure described by Wertz[49] and Cooper and Ziegler[50] using eqs 1−4.

$$\Delta S_1 = R \ln V^{s}_{m,liq}/V_{m,gas} \quad (1)$$

$$\Delta S_2 = R \ln V^{\circ}_{m}/V^{s}_{m,liq} \quad (2)$$

$$\alpha = \frac{S^{\circ,s}_{liq} - (S^{\circ,s}_{gas} + R \ln V^{s}_{m,liq}/V_{m,gas})}{(S^{\circ,s}_{gas} + R \ln V^{s}_{m,liq}/V_{m,gas})} \quad (3)$$

$$\begin{aligned} S_s &= S_g + \Delta S_{sol} \\ &= S_g + [\Delta S_1 + \alpha(S_g + \Delta S_1) + \Delta S_2] \\ &= S_g + [(-11.80\ \text{cal/mol·K}) - 0.21 \\ &\quad \times (S_g - 11.80\ \text{cal/mol·K}) + 5.45\ \text{cal/mol·K}] \end{aligned} \quad (4)$$

where S_g is the gas-phase entropy of solute, ΔS_{sol} is the solvation entropy, $S^{\circ,s}_{liq}$, $S^{\circ,s}_{gas}$, and $V^{s}_{m,liq}$ are the standard entropies and molar volume of the solvent in liquid or gas phases (174.5 and 270.3 J/mol·K and 64.15 mL/mol, respectively, for CH_2Cl_2), $V_{m,gas}$ is the molar volume of the ideal gas at 25 °C (24 450 mL/mol), and V°_{m} is the molar volume of the solution corresponding to the standard conditions (1000 mL/mol). The enthalpies and Gibbs free energies in solution (H_s and G_s) were estimated using the expressions 5 and 6

$$\begin{aligned} H_s &= E_s(\text{6-311+G(d, p)}) + H_g(\text{6-31G(d)}) \\ &\quad - E_g(\text{6-311+G(d, p)}) \end{aligned} \quad (5)$$

$$G_s = H_s - TS_s \quad (6)$$

where E_s, E_g, and H_g are the total energies in solution and in gas phase, and gas-phase enthalpy is calculated at the corresponding level.

The Wiberg bond indices (B_i)[51] were computed by using the natural bond orbital partitioning scheme.[52] The reaction synchronicity (S_y) was calculated using the formulas reported previously.[53−56] The S_y values vary from 0 to 1; for perfectly synchronous reactions S_y = 1; for stepwise CAs S_y = 0.

Our previous theoretical studies[14,26,28−30] indicated that both acyclic and cyclic nitrones couple with MeCN or complex **I** via a concerted mechanism, while the stepwise routes are greatly disfavored. Hence, in this work only the concerted pathways are examined.

Synthetic Work. *Synthesis of (2,3-Dihydro-1,2,4-oxadiazole)-(nitrile)Pt^{II} Complexes (a General Procedure).* The solutions of each of nitrones **5**−**8** (0.1 mmol) in $CHCl_3$ (1 mL) were added to a solution of each of **1**−**4** (0.1 mmol) in $CHCl_3$ (1 mL). The mixture was stirred at room temperature for 5 h (at −15 °C for 2 d when nitrone **8** was used); the progress of the reaction was monitored by TLC. The separation of **9**−**24** was achieved by column chromatography on SiO_2 (the first fraction; eluent $CHCl_3/Me_2CO$, 10:1, v/v). The solvent was evaporated *in vacuo* at 20−25 °C to give yellow, oily residues. The residues were crystallized under *n*-hexane to form the yellow powders of **9**−**24**. The complexes were dried in air at 20−25 °C. Yields: 78−81%.

9 (52.6 mg, 81%). Anal. Found: C, 46.29; H, 3.87; N, 6.47 (calcd for $C_{25}H_{25}N_3Cl_2OPt$: C, 46.23; H, 3.88; N, 6.47); m/z (high-resolution ESI^+) 671.0920 ($[M + Na]^+$, requires 671.0921); R_f = 0.37 (eluent $CHCl_3/Me_2CO$, 30:1, v/v); ν_{max} (KBr)/cm^{-1} 2934 m (C−H), 1636 s (C═N); δ_H (300 MHz, $CDCl_3$) 1.34 (3H, t, J = 7.6 Hz, CH_3 from Et of the 2,3-dihydro-1,2,4-oxadiazole ligand), 1.57 (3H, s, CH_3 from Et of the nitrile ligand), 2.19 (2H, s, CH_2 from Et of the nitrile

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ligand), 2.93 (2H, q, J = 7.6 Hz, CH_2 from Et of the 2,3-dihydro-1,2,4-oxadiazole ligand) 6.70, 7.01, 7.30, and 7.56 (15H, 4 m, $H_{aromatic}$); δ_C (75.5 MHz, $CDCl_3$) 9.9 and 10.3 (CH_3 from Et of the nitrile and the 2,3-dihydro-1,2,4-oxadiazole ligands), 13.1 (CH_2 from Et of the nitrile ligand), 22.6 (CH_2 from Et of the 2,3-dihydro-1,2,4-oxadiazole ligand), 98.2 (N−C−N), 121.2, 126.1, 126.9, 128.2, 128.8, 132.3, 138.1, and 144.5 ($C_{aromatic}$), 159.6 (C(O)═N); the C≡N carbon was not detected.

10 (52.3 mg, 80%). Anal. Found: C, 47.07; H, 4.12; N, 6.33 (calcd for $C_{26}H_{27}N_3Cl_2OPt$: C, 47.07; H, 4.10; N, 6.33); *m/z* (high-resolution ESI$^+$) 701.0819 ($[M + K]^+$, requires 701.0816); R_f = 0.41 (eluent $CHCl_3/Me_2CO$, 30:1, v/v); ν_{max} (KBr)/cm^{-1} 2934 m (C−H), 1637 s (C═N); δ_H (300 MHz, $CDCl_3$): 1.29 (3H, t, *J* = 7.6 Hz, CH_3 from Et of the 2,3-dihydro-1,2,4-oxadiazole ligand), 1.57 (3H, s, CH_3 from Et of the nitrile ligand), 2.14 (3H, s, CH_3 from C_6H_4Me-*p*), 2.19 (2H, s, CH_2 from Et of the nitrile ligand), 2.81 (2H, q, *J* = 7.6 Hz, CH_2 from Et of the 2,3-dihydro-1,2,4-oxadiazole ligand), 6.46 (2H, d, *o*-protons from C_6H_4Me-*p*), 6.70 (2H, d, *m*-protons from C_6H_4Me-*p*), 7.27 and 7.50 (10H, 2 m, $H_{aromatic}$); δ_C (75.5 MHz, $CDCl_3$) 9.9 and 10.3 (CH_3 from Et of the nitrile and the 2,3-dihydro-1,2,4-oxadiazole ligand), 13.1 (CH_2 from Et of the nitrile ligand), 21.2 (CH_3 from C_6H_4Me-*p*), 23.2 (CH_2 from Et of the 2,3-dihydro-1,2,4-oxadiazole ligand), 99.1 (N−C−N), 121.0, 124.8, 127.5, 129.0, 129.5, 131.5, 135.0, and 141.1 ($C_{aromatic}$), 162.2 (C(O)═N); the C≡N carbon was not detected.

11 (52.2 mg, 81%). Anal. Found: C, 43.90; H, 3.55; N, 6.16 (calcd for $C_{25}H_{24}N_3Cl_3OPt$: C, 43.90; H, 3.54; N, 6.14); *m/z* (high-resolution ESI$^+$) 683.0711 ($[M + H]^+$, requires 683.0711); R_f = 0.40 (eluent $CHCl_3/Me_2CO$, 30:1, v/v); ν_{max} (KBr)/cm^{-1}: 2936 m (C−H), 1636 s (C═N); δ_H (300 MHz, $CDCl_3$) 1.30 (3H, t, *J* = 7.6 Hz, CH_3 from Et of the 2,3-dihydro-1,2,4-oxadiazole ligand), 1.57 (3H, s, CH_3 from Et of the nitrile ligand), 2.19 (2H, s, CH_2 from Et of the nitrile ligand), 2.82 (2H, q, *J* = 7.6 Hz, CH_2 from Et of the 2,3-dihydro-1,2,4-oxadiazole ligand), 6.49 (2H, d, *o*-protons from C_6H_4Cl-*p*), 6.88 (2H, d, *m*-protons from C_6H_4Cl-*p*), 7.32 and 7.50 (10H, 2 m, $H_{aromatic}$), δ_C (75.5 MHz, $CDCl_3$) 9.9 and 10.3 (CH_3 from Et of the nitrile and the 2,3-dihydro-1,2,4-oxadiazole ligand), 13.1 (CH_2 from Et of the nitrile ligand), 22.6 (CH_2 from Et of the 2,3-dihydro-1,2,4-oxadiazole ligand), 98.2 (N−C−N), 122.8, 127.3, 126.9, 128.5, 129.2, 132.0, 137.7, and 143.0 ($C_{aromatic}$), 159.6 (C(O)═N); the C≡N carbon was not detected.

12 (54.1 mg, 80%). Anal. Found: C, 46.01; H, 4.03; N, 6.24 (calcd for $C_{26}H_{27}N_3Cl_2O_2Pt$: C, 46.96; H, 4.01; N, 6.18); *m/z* (high-resolution ESI$^+$) 717.0761 ($[M + K]^+$, requires 717.0765); R_f = 0.41 (eluent $CHCl_3/Me_2CO$, 30:1, v/v); ν_{max} (KBr)/cm^{-1} 2934 m (C−H), 1637 s (C═N); δ_H (300 MHz, $CDCl_3$) 1.29 (3H, t, *J* = 7.6 Hz, CH_3 from Et of the 2,3-dihydro-1,2,4-oxadiazole ligand), 1.57 (3H, s, CH_3 from Et of the nitrile ligand), 2.19 (2H, s, CH_2 from Et of the nitrile ligand), 2.81 (2H, q, *J* = 7.6 Hz, CH_2 from Et of the 2,3-dihydro-1,2,4-oxadiazole ligand), 3.72 (3H, s, CH_3 from *p*-$MeOC_6H_4$), 6.62 (2H, d, *o*-protons from *p*-$MeOC_6H_4$), 6.77 (2H, d, *m*-protons from *p*-$MeOC_6H_4$), 7.23 and 7.53 (10H, 2 m, $H_{aromatic}$); δ_C (75.5 MHz, $CDCl_3$) 9.9 and 10.2 (CH_3 from Et of the nitrile and the 2,3-dihydro-1,2,4-oxadiazole ligand), 13.3 (CH_2 from Et of the nitrile ligand), 23.2 (CH_2 from Et of the 2,3-dihydro-1,2,4-oxadiazole ligand), 62.0 (CH_3 from *p*-$MeOC_6H_4$), 98.4 (N−C−N), 122.1, 127.2, 129.1, 129.2, 132.4, 136.3, 137.7, and 141.2 ($C_{aromatic}$), 161.2 (C(O)═N); the C≡N carbon was not detected.

13 (54.8 mg, 81%). Anal. Found: C, 44.20; H, 4.05; N, 10.33 (calcd for $C_{25}H_{27}N_5Cl_2OPt$: C, 44.19; H, 4.01; N, 10.31); *m/z* (high-resolution ESI$^+$) 680.1374 ($[M + H]^+$, requires 680.1240); R_f = 0.38 (eluent $CHCl_3/Me_2CO$, 30:1, v/v); ν_{max} (KBr)/cm^{-1} 2922 m (C−H), 2305 s (C≡N), 1663 s (C═N); δ_H (300 MHz, $CDCl_3$) 2.87 (6H, s, NMe_2 of the nitrile ligand), 3.82 (6H, br s, NMe_2 of the 2,3-dihydro-1,2,4-oxadiazole ligand), 6.70, 7.01, 7.35, and 7.58 (15H, 4 m, $H_{aromatic}$); δ_C (75.5 MHz, $CDCl_3$): 40.3, 40.4 (NMe_2 of the 2,3-dihydro-1,2,4-oxadiazole ligand and of the nitrile ligand), 98.3 (N−C−N), 121.6, 126.3, 127.2, 128.4, 129.1, 132.0, 137.9, and 144.2 ($C_{aromatic}$), 161.2 (C(O)═N); the C≡N carbon was not detected.

14 (55.9 mg, 81%). Anal. Found: C, 45.05; H, 4.21; N, 10.10 (calcd for $C_{26}H_{29}N_5Cl_2OPt$: C, 45.03; H, 4.21; N, 10.10); *m/z* (high-resolution ESI$^+$) 693.1477 ($[M + H]^+$, requires 693.1475), 716.1306 ($[M + Na]^+$, requires 716.5147); R_f = 0.39 (eluent $CHCl_3/Me_2CO$, 30:1, v/v); ν_{max} (KBr)/cm^{-1} 2923 m (C−H), 2301 m (C≡N), 1665 s (C═N); δ_H (300 MHz, $CDCl_3$) 2.20 (3H, s, CH_3 from C_6H_4Me-*p*), 2.86 (6H, s, NMe_2 of the nitrile ligand), 3.75 (6H, br s, NMe_2 of the 2,3-dihydro-1,2,4-oxadiazole ligand), 6.57 (2H, d, *o*-protons from C_6H_4Me-*p*), 6.83 (2H, d, *m*-protons from C_6H_4Me-*p*), 7.28 and 7.56 (10H, 2 m, $H_{aromatic}$); δ_C (75.5 MHz, $CDCl_3$) 21.3 (CH_3 from C_6H_4Me-*p*), 40.3, 40.4 (NMe_2 of the 2,3-dihydro-1,2,4-oxadiazole ligand and of the nitrile ligand), 98.1 (N−C−N), 121.9, 127.2, 128.9, 129.0, 132.0, 136.2, 137.9, and 141.5 ($C_{aromatic}$), 161.4 (C(O)═N); the C≡N carbon was not detected.

15 (57.5 mg, 81%). Anal. Found: C, 42.09; H, 3.67; N, 9.85 (calcd for $C_{25}H_{26}N_5Cl_3OPt$: C, 42.06; H, 3.67; N, 9.81); *m/z* (high-resolution ESI$^+$) 735.0742 ($[M + Na]^+$, requires 735.0748); R_f = 0.42 (eluent $CHCl_3/Me_2CO$, 30:1, v/v); ν_{max} (KBr)/cm^{-1} 2929 m (C−H), 2293 m (C≡N), 1669 s (C═N); δ_H (300 MHz, $CDCl_3$) 2.88 (6H, s, NMe_2 of the nitrile ligand), 3.76 (6H, br s, NMe_2 of the 2,3-dihydro-1,2,4-oxadiazole ligand), 6.63 (2H, d, *o*-protons from C_6H_4Cl-*p*), 6.99 (2H, d, *m*-protons from C_6H_4Cl-*p*), 7.32 and 7.58 (10H, 2 m, $H_{aromatic}$); δ_C (75.5 MHz, $CDCl_3$) 40.3, 40.4 (NMe_2 of the 2,3-dihydro-1,2,4-oxadiazole ligand and of the nitrile ligand), 98.3 (N−C−N), 122.9, 127.4, 128.5, 129.3, 131.7, 131.9, 137.5, and 142.8 ($C_{aromatic}$), 161.2 (C(O)═N); the C≡N carbon was not detected.

16 (53.3 mg, 78%). Anal. Found: C, 44.03; H, 4.12; N, 9.87 (calcd for $C_{26}H_{29}N_5Cl_2O_2Pt$: C, 44.01; H, 4.12; N, 9.87); *m/z* (high-resolution ESI$^+$) 731.1248 ($[M + Na]^+$, requires 731.1244); R_f = 0.38 (eluent $CHCl_3/Me_2CO$, 30:1, v/v); ν_{max} (KBr)/cm^{-1} 2923 m (C−H), 2301 m (C≡N), 1665 s (C═N); δ_H (300 MHz, $CDCl_3$) 2.86 (6H, s, NMe_2 of the nitrile ligand), 3.70 (3H, s, CH_3 from *p*-$MeOC_6H_4$), 3.76 (6H, br s, NMe_2 of the 2,3-dihydro-1,2,4-oxadiazole ligand), 6.60 (2H, d, *o*-protons from *p*-$MeOC_6H_4$), 6.79 (2H, d, *m*-protons from *p*-$MeOC_6H_4$), 7.25 and 7.57 (10H, 2 m, $H_{aromatic}$); δ_C (75.5 MHz, $CDCl_3$) 40.3, 40.4 (NMe_2 of the 2,3-dihydro-1,2,4-oxadiazole ligand and of the nitrile ligand), 61.9 (CH_3 from *p*-$MeOC_6H_4$), 98.2 (N−C−N), 122.1, 127.2, 128.8, 129.1, 132.1, 136.3, 137.7, and 141.5 ($C_{aromatic}$), 161.3 (C(O)═N); the C≡N carbon was not detected.

17 (59.0 mg, 80%). Anal. Found: C, 47.36; H, 4.81; N, 9.50 (calcd for $C_{29}H_{35}N_5Cl_2OPt$: C, 47.35; H, 4.80; N, 9.52); *m/z* (high-resolution ESI$^+$) 757.1765 ($[M + Na]^+$, requires 757.1764); R_f = 0.41 (eluent $CHCl_3/Me_2CO$, 30:1, v/v); ν_{max} (KBr)/cm^{-1} 2976 m (C−H), 2289 m (C≡N), 1649 s (C═N); δ_H (300 MHz, $CDCl_3$) 1.22 (6H, t, *J* = 7.4 Hz, CH_3 from NEt_2 of the nitrile ligand), 1.51 (6H, br s, CH_3 from NEt_2 of the 2,3-dihydro-1,2,4-oxadiazole ligand), 3.09 (4H, q, *J* = 7.4 Hz, CH_2 from NEt_2 of the nitrile ligand), 4.36 (4H, br s, CH_2 from NEt_2 of the 2,3-dihydro-1,2,4-oxadiazole ligand), 6.70, 7.01, 7.30, and 7.56 (15H, 4 m, $H_{aromatic}$) δ_C (75.5 MHz, $CDCl_3$): 12.9 (CH_3 from NEt_2 of the nitrile ligand), 13.7 (6H, t, CH_3 from NEt_2 of the 2,3-dihydro-1,2,4-oxadiazole ligand), 44.4 (CH_2 from NEt_2 of the nitrile ligand), 46.2 (CH_2 from NEt_2 of the 2,3-dihydro-1,2,4-oxadiazole ligand), 98.2 (N−C−N), 121.2, 126.0, 126.9, 128.3, 128.8, 132.2, 138.1, and 144.4 ($C_{aromatic}$), 159.6 (C(O)═N); the C≡N carbon was not detected.

18 (60.3 mg, 81%). Anal. Found: C, 48.14; H, 4.94; N, 9.35 (calcd for $C_{30}H_{37}N_5Cl_2OPt$: C, 48.06; H, 4.97; N, 9.34); *m/z* (high-resolution ESI$^+$) 749.2101 ($[M + H]^+$, requires 749.2101); R_f = 0.38 (eluent $CHCl_3/Me_2CO$, 30:1, v/v); ν_{max} (KBr)/cm^{-1} 2977 m (C−H), 2289 m (C≡N), 1648 s (C═N); δ_H (300 MHz, $CDCl_3$) 1.20 (6H, t, *J* = 7.3 Hz, CH_3 from NEt_2 of the nitrile ligand), 1.49 (6H, br s, CH_3 from NEt_2 of the 2,3-dihydro-1,2,4-oxadiazole ligand), 2.20 (3H, s, CH_3 from C_6H_4Me-*p*), 3.06 (4H, q, *J* = 7.3 Hz, CH_2 from NEt_2 of the nitrile ligand), 4.34 (4H, br s, CH_2 from NEt_2 of the 2,3-dihydro-1,2,4-oxadiazole ligand), 6.69 (2H, d, *o*-protons from C_6H_4Me-*p*), 6.80 (2H, d, *m*-protons from C_6H_4Me-*p*), 7.28 and 7.58 (10H, 2 m, $H_{aromatic}$); δ_C (75.5 MHz, $CDCl_3$) 13.1 (CH_3 from NEt_2 of the nitrile ligand), 14.0 (CH_3 from NEt_2 of the 2,3-dihydro-1,2,4-oxadiazole ligand), 21.3 (CH_3 from C_6H_4Me-*p*), 44.4 (CH_2 from NEt_2 of the nitrile ligand), 46.0 (CH_2 from NEt_2 of the 2,3-dihydro-1,2,4-oxadiazole ligand), 98.2

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(N−C−N), 121.8, 127.0, 128.9, 132.2, 136.0, 138.1, and 144.7 ($C_{aromatic}$), 159.9 (C(O)=N); the C≡N carbon was not detected.

19 (62.2 mg, 81%). Anal. Found: C, 45.21; H, 4.46; N, 9.15) (calcd for $C_{29}H_{34}N_5C_3OPt$: C, 45.23; H, 4.45; N, 9.09); *m/z* (high-resolution ESI$^+$) 769.1553 ($[M + H]^+$, requires 769.1555); R_f = 0.40 (eluent $CHCl_3/Me_2CO$, 30:1, v/v); ν_{max} (KBr)/cm^{-1} 2979 m (C−H), 2287 m (C≡N), 1649 s (C=N); δ_H (300 MHz, $CDCl_3$) 1.20 (6H, t, J = 7.3 Hz, CH_3 from NEt_2 of the nitrile ligand), 1.49 (6H, br s, CH_3 from NEt_2 of the 2,3-dihydro-1,2,4-oxadiazole ligand), 3.06 (4H, q, J = 7.3 Hz, CH_2 from NEt_2 of the nitrile ligand), 4.39 (4H, br s, CH_2 from NEt_2 of the 2,3-dihydro-1,2,4-oxadiazole ligand), 6.67 (2H, d, *o*-protons fromC_6H_4Cl-*p*), 6.97 (2H, d, *m*-protons fromC_6H_4Cl-*p*), 7.33 and 7.58 (10H, 2 m, $H_{aromatic}$); δ_C (75.5 MHz, $CDCl_3$) 13.1 (CH_3 from NEt_2 of the nitrile ligand), 13.9 (CH_3 from NEt_2 of the 2,3-dihydro-1,2,4-oxadiazole ligand), 44.5 (CH_2 from NEt_2 of the nitrile ligand), 46.3 (CH_2 from NEt_2 of the 2,3-dihydro-1,2,4-oxadiazole ligand), 98.2 (N−C−N), 122.8, 127.2, 126.9, 128.5, 129.1, 132.0, 137.8, and 143.0 ($C_{aromatic}$), 159.9 (C(O)=N); the C≡N carbon was not detected.

20 (60.1 mg, 79%). Anal. Found: C, 47.14; H, 4.91; N, 9.15 (calcd for $C_{30}H_{37}N_5Cl_2O_2Pt$: C, 47.06; H, 4.87; N, 9.15); *m/z* (high-resolution ESI$^+$) 765.2055 ($[M + H]^+$, requires 765.2050); R_f = 0.40 (eluent $CHCl_3/Me_2CO$, 30:1, v/v); ν_{max} (KBr)/cm^{-1} 2977 m (C−H), 2289 m (C≡N), 1648 s (C=N); δ_H (300 MHz, $CDCl_3$) 1.20 (6H, t, J = 7.3 Hz, CH_3 from NEt_2 of the nitrile ligand), 1.49 (6H, br s, CH_3 from NEt_2 of the 2,3-dihydro-1,2,4-oxadiazole ligand), 3.06 (4H, q, J = 7.3 Hz, CH_2 from NEt_2 of the nitrile ligand), 3.73 (3H, s, CH_3 from *p*-$MeOC_6H_4$), 4.34 (4H, br s, CH_2 from NEt_2 of the 2,3-dihydro-1,2,4-oxadiazole ligand), 6.63 (2H, d, *o*-protons from *p*-$MeOC_6H_4$), 6.79 (2H, d, *m*-protons from *p*-$MeOC_6H_4$), 7.25 and 7.55 (10H, 2 m, $H_{aromatic}$); δ_C (75.5 MHz, $CDCl_3$) 13.1 (CH_3 from NEt_2 of the nitrile ligand), 14.0 (CH_3 from NEt_2 of the 2,3-dihydro-1,2,4-oxadiazole ligand), 44.4 (CH_2 from NEt_2 of the nitrile ligand), 46.0 (CH_2 from NEt_2 of the 2,3-dihydro-1,2,4-oxadiazole ligand), 62.0 (CH_3 from *p*-$MeOC_6H_4$), 98.2 (N−C−N), 122.2, 127.2, 128.6, 129.2, 132.4, 136.3, 137.7, and 141.1 ($C_{aromatic}$), 161.3 (C(O)=N); the C≡N carbon was not detected.

21 (61.2 mg, 81%). Anal. Found: C, 49.08; H, 4.61; N, 9.24 (calcd for $C_{31}H_{35}N_5Cl_2OPt$: C, 49.01; H, 4.64; N, 9.22); *m/z* (high-resolution ESI$^+$) 781.1767 ($[M + Na]^+$, requires 781.1764); R_f = 0.37 (eluent $CHCl_3/Me_2CO$, 30:1, v/v); ν_{max} (KBr)/cm^{-1} 2976 m (C−H), 2289 m (C≡N), 1649 s (C=N); δ_H (300 MHz, $CDCl_3$) 1.59 (6H, br s, β- and γ-protons from NC_5H_{10} of the nitrile ligand), 1.76 (6H, br s, β- and γ-protons from NC_5H_{10} of the 2,3-dihydro-1,2,4-oxadiazole ligand), 3.19 (4H, q, J = 5.1 Hz, α-protons from NC_5H_{10} of the nitrile ligand), 4.39 (4H, br s, α-protons from NC_5H_{10} of the 2,3-dihydro-1,2,4-oxadiazole ligand), 6.70, 7.01, 7.30, and 7.54 (15H, 4 m, $H_{aromatic}$); δ_C (75.5 MHz, $CDCl_3$) 21.3 (γ-carbons from NC_5H_{10} of the nitrile ligand), 22.9 (γ-carbons from NC_5H_{10} of the 2,3-dihydro-1,2,4-oxadiazole ligand), 24.3 (β-carbons from NC_5H_{10} of the nitrile ligand), 22.9 (β-carbons from NC_5H_{10} of the 2,3-dihydro-1,2,4-oxadiazole ligand), 49.3 (α-carbons from NC_5H_{10} of the nitrile ligand), 49.9 (α-carbons from NC_5H_{10} of the 2,3-dihydro-1,2,4-oxadiazole ligand ligand), 98.2 (N−C−N), 121.1, 126.0, 126.9, 128.3, 128.6, 132.2, 138.1, and 144.4 ($C_{aromatic}$), 159.6 (C(O)=N); the C≡N carbon was not detected.

22 (61.9 mg, 80.1%). Anal. Found: C, 49.67; H, 4.82; N, 9.10 (calcd for $C_{32}H_{37}N_5Cl_2OPt$: C, 49.68; H, 4.82; N, 9.05); *m/z* (high-resolution ESI$^+$) 795.1920 ($[M + Na]^+$, requires 795.1921); R_f = 0.39 (eluent $CHCl_3/Me_2CO$, 30:1, v/v); ν_{max} (KBr)/cm^{-1} 2976 m (C−H), 2289 m (C≡N), 1649 s (C=N); δ_H (300 MHz, $CDCl_3$) 1.59 (6H, br s, β- and γ-protons from NC_5H_{10} of the nitrile ligand), 1.76 (6H, br s, β- and γ-protons from NC_5H_{10} of the 2,3-dihydro-1,2,4-oxadiazole ligand), 2.20 (3H, s, CH_3 from C_6H_4Me-*p*), 3.19 (4H, q, J = 5.09 Hz, α-protons from NC_5H_{10} of the nitrile ligand), 4.39 (4H, br s, α-protons from NC_5H_{10} of the 2,3-dihydro-1,2,4-oxadiazole ligand), 6.45 (2H, d, *o*-protons from C_6H_4Me-*p*), 6.71 (2H, d, *m*-protons from C_6H_4Me-*p*), 7.27 and 7.51 (10H, 2 m, $H_{aromatic}$); δ_C (75.5 MHz, $CDCl_3$) 21.1 and 21.2 (CH_3 from C_6H_4Me-*p* and γ-carbons from NC_5H_{10} of the nitrile ligand), 22.9 (γ-carbons from NC_5H_{10} of the 2,3-dihydro-1,2,4-oxadiazole ligand), 24.4 (β-carbons from NC_5H_{10} of the nitrile ligand), 22.9 (β-carbons from NC_5H_{10} of the 2,3-dihydro-1,2,4-oxadiazole ligand), 49.2 (α-carbons from NC_5H_{10} of the nitrile ligand), 49.8 (α-carbons from NC_5H_{10} of the 2,3-dihydro-1,2,4-oxadiazole ligand ligand), 98.6 (N−C−N), 121.1, 124.8, 127.6, 129.0, 129.6, 131.5, 135.2, and 141.3 ($C_{aromatic}$), 162.2 (C(O)=N); the C≡N carbon was not detected.

23 (64.0 mg, 81%). Anal. Found: C, 46.93; H, 4.35; N, 8.83 (calcd for $C_{31}H_{34}N_5Cl_3OPt$: C, 46.89; H, 4.32; N, 8.82); *m/z* (high-resolution ESI$^+$) 815.1372 ($[M + Na]^+$, requires 815.1374); R_f = 0.37 (eluent $CHCl_3/Me_2CO$, 30:1, v/v); ν_{max} (KBr)/cm^{-1} 2976 m (C−H), 2289 m (C≡N), 1649 s (C=N); δ_H (300 MHz, $CDCl_3$) 1.58 (6H, br s, β- and γ-protons from NC_5H_{10} of the nitrile ligand), 1.76 (6H, br s, β- and γ-protons from NC_5H_{10} of the 2,3-dihydro-1,2,4-oxadiazole ligand), 3.19 (4H, q, J = 5.1 Hz, α-protons from NC_5H_{10} of the nitrile ligand), 4.38 (4H, br s, α-protons from NC_5H_{10} of the 2,3-dihydro-1,2,4-oxadiazole ligand), 6.66 (2H, d, *o*-protons from C_6H_4Cl-*p*), 6.95 (2H, d, *m*-protons from C_6H_4Cl-*p*), 7.33 and 7.58 (10H, 2 m, $H_{aromatic}$); δ_C (75.5 MHz, $CDCl_3$) 21.2 (γ-carbons from NC_5H_{10} of the nitrile ligand), 22.9 (γ-carbons from NC_5H_{10} of the 2,3-dihydro-1,2,4-oxadiazole ligand), 24.3 (β-carbons from NC_5H_{10} of the nitrile ligand), 22.9 (β-carbons from NC_5H_{10} of the 2,3-dihydro-1,2,4-oxadiazole ligand), 49.2 (α-carbons from NC_5H_{10} of the nitrile ligand), 49.8 (α-carbons from NC_5H_{10} of the 2,3-dihydro-1,2,4-oxadiazole ligand ligand), 98.3 (N−C−N), 122.6, 127.2, 126.9, 128.5, 129.2, 132.1, 137.7, and 143.3 ($C_{aromatic}$), 159.7 (C(O)=N); the C≡N carbon was not detected.

24 (61.7 mg, 78%). Anal. Found: C, 48.70; H, 4.70; N, 8.87 (calcd for $C_{32}H_{37}N_5Cl_2O_2Pt$: C, 48.67; H, 4.72; N, 8.87); *m/z* (high-resolution ESI$^+$) 811.1877 ($[M + Na]^+$, requires 811.1870); R_f = 0.40 (eluent $CHCl_3/Me_2CO$, 30:1, v/v); ν_{max} (KBr)/cm^{-1} 2976 m (C−H), 2284 m (C≡N), 1649 s (C=N); δ_H (300 MHz, $CDCl_3$) 1.59 (6H, br s, β- and γ-protons from NC_5H_{10} of the nitrile ligand), 1.76 (6H, br s, β- and γ-protons from NC_5H_{10} of the 2,3-dihydro-1,2,4-oxadiazole ligand), 3.19 (4H, q, J = 5.1 Hz, α-protons from NC_5H_{10} of the nitrile ligand), 3.72 (3H, s, CH_3 from *p*-$MeOC_6H_4$), 4.39 (4H, br s, α-protons from NC_5H_{10} of the 2,3-dihydro-1,2,4-oxadiazole ligand), 6.56 (2H, d, *o*-protons from *p*-$MeOC_6H_4$), 6.74 (2H, d, *m*-protons from *p*-$MeOC_6H_4$), 7.25 and 7.53 (10H, 2 m, $H_{aromatic}$); δ_C (75.5 MHz, $CDCl_3$) 21.1 (γ-carbons from NC_5H_{10} of the nitrile ligand), 22.9 (γ-carbons from NC_5H_{10} of the 2,3-dihydro-1,2,4-oxadiazole ligand), 24.4 (β-carbons from NC_5H_{10} of the nitrile ligand), 22.9 (β-carbons from NC_5H_{10} of the 2,3-dihydro-1,2,4-oxadiazole ligand), 49.2 (α-carbons from NC_5H_{10} of the nitrile ligand), 49.8 (α-carbons from NC_5H_{10} of the 2,3-dihydro-1,2,4-oxadiazole ligand ligand), 62.1 (CH_3 from *p*-$MeOC_6H_4$), 98.6 (N−C−N), 122.1, 127.3, 129.1, 129.3, 132.0, 136.1, 137.5, and 141.2 ($C_{aromatic}$), 161.3 (C(O)=N); the C≡N carbon was not detected.

*Synthesis of (2,3-Dihydro-1,2,4-oxadiazole)$_2$Pt^{II} Complexes (**25**−**27** and **29**−**31**).* The solutions of each of nitrones **5**−**7** (0.2 mmol) in $CHCl_3$ (1 mL) were added to a solution of the corresponding *trans*-$[PtCl_2(NCR)_2]$ (0.1 mmol; R = Et, NMe_2) in $CHCl_3$ (1 mL). The mixture was stirred at 35 °C for 5 h, and the progress of the reaction was monitored by TLC. The yellow precipitates of **25**−**27** and **29**−**31** were separated by filtration and washed by *n*-hexane (three 1 mL portions). The complexes were dried in air at 20−25 °C. Yields: 89−90%.

34, 35, 38, and 39. The solutions of each of nitrones **6** and **7** (0.2 mmol) in THF (1 mL) were added to a solution of the corresponding *trans*-$[PtCl_2(NCR)_2]$ (0.1 mmol; R = NEt_2, $N(C_5H_{10})$) in THF (1 mL). The mixture was stirred at 35 °C for 5 h, and the progress of the reaction was monitored by TLC. The yellow precipitates of **34**, **35**, **38**, and **39** were separated by filtration and washed by *n*-hexane (three 1 mL portions). The complexes were dried in air at 20−25 °C. Yields: 88−90%.

33 and 37. The solution of nitrone **5** (1.4 mmol) in $CHCl_3$ (1 mL) was added to a solution of the corresponding *trans*-$[PtCl_2(NCR)_2]$ (0.1 mmol; R = NEt_2, $N(C_5H_{10})$) in $CHCl_3$ (1 mL). The mixture was stirred at 35 °C for 5 h, and the progress of the reaction was monitored by TLC. The separation of **33** and **37** was achieved by column chromatography on SiO_2 (the first fraction; eluent $CHCl_3/Me_2CO$, 10:1, v/v). The solvent was evaporated *in vacuo* at 20−25 °C

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to give yellow, oily residues. The residues were crystallized under *n*-hexane to form the yellow powders of **33** and **37**. The complexes were dried in air at 20−25 °C. Yields: 76−79%.

28, 32, 36, and 40. The solution of nitrone **8** (1.4 mmol) in $CHCl_3$ (1 mL) was added to a solution of each of **1**−**4** (0.1 mmol) in $CHCl_3$ (1 mL). The mixture was stirred at −15 °C for 4 h, and the progress of the reaction was monitored by TLC. After the total conversion of the starting complexes into corresponding mono-CAs (3−4 h), the reaction mixture was stirred for 5 h at 35 °C. The separation of **28**, **32**, **36**, or **40** was achieved by column chromatography on SiO_2 (the first fraction; eluent $CHCl_3/Me_2CO$, 10:1, v/v). The solvent was evaporated *in vacuo* at 20−25 °C to give yellow, oily residues. The residues were crystallized under a layer of *n*-hexane to form the yellow powders of **28**, **32**, **36**, or **40**. The complexes were dried in air at 20−25 °C. Yields: 78−80%.

25 (81.7 mg, 89%). Anal. Found: C, 57.33; H, 4.38; N, 6.05 (calcd for $C_{44}H_{40}N_4Cl_2O_2Pt$: C, 57.27; H, 4.37; N, 6.07); *m*/*z* (high-resolution ESI$^+$) 960.1810 ([M + K]$^+$, requires 960.1813); R_f = 0.57 (eluent $CHCl_3/Me_2CO$, 40:1, v/v); ν_{max} (KBr)/cm^{-1} 2934 m (C−H), 1636 s (C═N); δ_H (300 MHz, CD_2Cl_2) 1.34 (6H, t, *J* = 7.6, CH_3 from Et), 2.93 (4H, q, *J* = 7.6, CH_2 from Et), 6.60, 6.94, 7.32, and 7.50 (30H, 4 m, $H_{aromatic}$); δ_C (75.5 MHz, CD_2Cl_2) 9.9 (CH_3 from Et), 22.6 (CH_2 from Et), 98.4 (N−C−N), 120.6, 126.0, 127.2, 128.3, 128.4, 129.1, 131.7, and 136.1 ($C_{aromatic}$), 160.1 (C(O)═N).

26 (85.2 mg, 90%). Anal. Found: 58.11; H, 4.66; N, 5.89 (calcd for $C_{46}H_{44}N_4Cl_2O_2Pt$: C, 58.11; H, 4.66; N, 5.89); *m*/*z* (high-resolution ESI$^+$) 972.2380 ([M + Na]$^+$, requires 972.2387); R_f = 0.58 (eluent $CHCl_3/Me_2CO$, 40:1, v/v); ν_{max} (KBr)/cm^{-1} 2934, 2978 m (C−H), 1643 s (C═N); δ_H (300 MHz, $CDCl_3$) 1.30 (6H, t, *J* = 7.6 Hz, CH_3 from Et), 2.14 (6H, s, CH_3 from C_6H_4Me-*p*), 2.81 (4H, q, *J* = 7.6 Hz, CH_2 from Et), 6.46 (4H, d, *o*-protons from C_6H_4Me-*p*), 6.70 (4H, d, *m*-protons from C_6H_4Me-*p*), 7.28 and 7.50 (20H, 2 m, $H_{aromatic}$); δ_C (75.5 MHz, CD_2Cl_2) 9.9 (CH_3 from Et), 21.2 (CH_3 from C_6H_4Me-*p*), 22.6 (CH_2 from Et), 98.3 (N−C−N),122.1, 126.7, 128.6, 128.8, 132.8, 135.8, 138.2, and 141.3 ($C_{aromatic}$), 161.1 (C(O)═N).

27 (88.5 mg, 90%). Found: C, 53.32; H, 3.88; N, 5.70 (calcd for $C_{44}H_{38}N_4Cl_4O_2Pt$: C, 53.29; H, 3.86; N, 5.65); *m*/*z* (high-resolution ESI$^+$) 990.1471 ([M + H]$^+$, requires 990.1475); R_f = 0.57 (eluent $CHCl_3/Me_2CO$, 40:1, v/v); R_f = 0.60 (eluent $CHCl_3/Et_2O$, 40/1.5, v/v); ν_{max} (KBr)/cm^{-1} 2934 m (C−H), 1637 s (C═N); δ_H (300 MHz, $CDCl_3$) 1.30 (6H, t, *J* = 7.6 Hz, CH_3 from Et), 2.82 (4H, q, *J* = 7.6 Hz, CH_2 from Et), 6.49 (4H, d, *o*-protons from C_6H_4Cl-*p*), 6.88 (4H, d, *m*-protons from C_6H_4Cl-*p*), 7.32 and 7.50 (20H, 2 m, $H_{aromatic}$), δ_C (75.5 MHz, $CDCl_3$) 9.9 (CH_3 from Et), 22.6 (CH_2 from Et), 98.4 (N−C−N), 123.3, 127.2, 128.3, 131.5, 132.7, 137.8, and 142.9 ($C_{aromatic}$), 160.1 (C(O)═N).

28 (76.7 mg, 78%). Anal. Found: C, 56.18; H, 4.53; N, 5.70 (calcd for $C_{46}H_{44}N_4Cl_2O_4Pt$: C, 56.21; H, 4.51; N, 5.70); *m*/*z* (high-resolution ESI$^+$) 1004.2883 ([M + Na]$^+$, requires 1004.2885); R_f = 0.60 (eluent $CHCl_3/Me_2CO$, 40/1, v/v); ν_{max} (KBr)/cm^{-1} 2934, 2978 m (C−H), 1643 s (C═N); δ_H (300 MHz, $CDCl_3$) 1.30 (6H, t, *J* = 7.6 Hz, CH_3 from Et), 2.81 (4H, q, *J* = 7.6 Hz, CH_2 from Et), 3.71 (3H, s, CH_3 from *p*-$MeOC_6H_4$), 6.46 (4H, d, *o*-protons from *p*-$MeOC_6H_4$), 6.70 (4H, d, *m*-protons from *p*-$MeOC_6H_4$), 7.28 and 7.50 (20H, 2 m, $H_{aromatic}$); δ_C (75.5 MHz, CD_2Cl_2) 9.9 (CH_3 from Et), 22.5 (CH_2 from Et), 61.9 ($CH_3$from *p*-$MeOC_6H_4$), 98.3 (N−C−N), 122.2, 127.0, 128.6, 128.7, 132.1, 136.8, 138.5, and 141.3 ($C_{aromatic}$), 161.2 (C(O)═N).

29 (83.2 mg, 87%). Anal. Found: C, 55.49; H, 4.40; N, 8.85 (calcd for $C_{44}H_{42}N_6Cl_2O_2Pt$: C, 55.46; H, 4.44; N, 8.82); *m*/*z* (high-resolution ESI$^+$) 990.2035 ([M + K]$^+$, requires 990.2031); R_f = 0.57 (eluent $CHCl_3/Me_2CO$, 40/1, v/v); ν_{max} (KBr)/cm^{-1} 2924 m (C−H), 1667 s (C═N); δ_H (300 MHz, $CDCl_3$) 3.06 (12H, br s, NMe_2), 6.43, 6.92, 7.22, and 7.45 (30H, 4 m, $H_{aromatic}$); δ_C (75.5 MHz, $CDCl_3$) 39.6 (NMe_2), 98.5 (N−C−N), 121.6, 126.1, 127.0, 128.3, 128.8, 132.5, 137.9, and 144.0 ($C_{aromatic}$), 160.4 (C(O)═N).

30 (87.7 mg, 90%). Found: C, 56.33; H, 4.70; N, 8.61 (calcd for $C_{46}H_{46}N_6Cl_2O_2Pt$: C, 56.32; H, 4.73; N, 8.57); *m*/*z* (high-resolution ESI$^+$) 1018.2332 ([M + K]$^+$, requires 1018.2344); R_f = 0.60 (eluent $CHCl_3/Me_2CO$, 40/1, v/v); ν_{max} (KBr)/cm^{-1} 2925 m (C−H), 1642 s (C═N); δ_H (300 MHz, CD_2Cl_2) 2.20 (6H, s, CH_3 from C_6H_4Me-*p*), 3.04 (12H, br s, NMe_2), 6.34 (4H, d, *o*-protons from C_6H_4Me-*p*), 6.77 (4H, d, *m*-protons from C_6H_4Me-*p*), 7.29 and 7.42 (20H, 2 m, $H_{aromatic}$); δ_C (75.5 MHz, $CDCl_3$) 21.3 (CH_3 from C_6H_4Me-*p*), 39.6 (NMe_2), 98.3 (N−C−N), 122.2, 126.8, 128.6, 128.7, 132.8, 135.9, 138.2, and 141.5 ($C_{aromatic}$), 161.2 (C(O)═N).

31 (90.6 mg, 90%). Anal. Found: C, 51.71; H, 3.98; N, 8.22 (calcd for $C_{44}H_{40}N_6Cl_4O_2Pt$: C, 51.72; H, 3.95; N, 8.23); *m*/*z* (high-resolution ESI$^+$) 1058.1250 ([M + K]$^+$, requires 1058.1252); R_f = 0.58 (eluent $CHCl_3/Me_2CO$, 40:1, v/v); ν_{max} (KBr)/cm^{-1} 2926 m (C−H), 1665 s (C═N); δ_H (300 MHz, CD_2Cl_2) 3.05 (12H, br s, NMe_2), 6.40 (4H, d, *o*-protons from C_6H_4Cl-*p*), 6.94 (4H, d, *m*-protons from C_6H_4Cl-*p*), 7.29 and 7.43 (20H, 2 m, $H_{aromatic}$); δ_C (75.5 MHz, $CDCl_3$) 39.6 (NMe_2), 98.6 (N−C−N), 123.0, 127.2, 128.4, 128.8, 132.5, 137.6, and 142.7 ($C_{aromatic}$), 166.8 (C(O)═N).

32 (80.5 mg, 80%). Found: C, 54.54; H, 4.60; N, 8.28 (calcd for $C_{46}H_{46}N_6Cl_2O_4Pt$: C, 54.55; H, 4.58; N, 8.30); *m*/*z* (high-resolution ESI$^+$) 1050.2242 ([M + K]$^+$, requires 1050.2242); R_f = 0.58 (eluent $CHCl_3/Me_2CO$, 40:1, v/v); ν_{max} (KBr)/cm^{-1} 2925 m (C−H), 1642 s (C═N); δ_H (300 MHz, CD_2Cl_2) 3.04 (12H, br s, NMe_2), 3.65 (6H, s, CH_3 from *p*-$MeOC_6H_4$), 6.31 (4H, d, *o*-protons from *p*-$MeOC_6H_4$), 6.79 (4H, d, *m*-protons from *p*-$MeOC_6H_4$), 7.31 and 7.40 (20H, 2 m, $H_{aromatic}$); δ_C (75.5 MHz, $CDCl_3$) 39.6 (NMe_2), 61.9 (CH_3 from *p*-$MeOC_6H_4$), 98.3 (N−C−N), 122.2, 126.8, 128.6, 128.7, 132.8, 135.9, 138.2, and 141.5 ($C_{aromatic}$), 161.2 (C(O)═N).

33 (79.6 mg, 79%). Anal. Found: C, 57.21; H, 5.03; N, 8.33 (calcd for $C_{48}H_{50}N_6Cl_2O_2Pt$: C, 57.14; H, 5.00; N, 8.33); *m*/*z* (high-resolution ESI$^+$) 1046.2651 ([M + K]$^+$, requires 1046.2657); R_f = 0.61 (eluent $CHCl_3/Me_2CO$, 40:1, v/v); ν_{max} (KBr)/cm^{-1} 2924 m (C−H), 1667 s (C═N); δ_H (300 MHz, $CDCl_3$) 1.08 (12H, t, *J* = 6.9 Hz, CH_3 from NEt_2), 3.61 (8H, br s, CH_2 from NEt_2), 6.42, 6.93, 7.20, and 7.47 (30H, 4 m, $H_{aromatic}$); δ_C (75.5 MHz, $CDCl_3$) 14.1 (CH_3 from NEt_2), 43.7 (CH_2 from NEt_2), 98.5 (N−C−N), 121.6, 126.1, 127.1, 128.2, 129.0, 132.5, 137.8, and 144.1 ($C_{aromatic}$), 160.5 (C(O)═N).

34 (92.2 mg, 89%). Found: C, 57.91; H, 5.25; N, 8.10 (calcd for $C_{50}H_{54}N_6Cl_2O_2Pt$: C, 57.91; H, 5.25; N, 8.10); *m*/*z* (high-resolution ESI$^+$) 1035.3331 ([M + K]$^+$, requires 1035.3333); R_f = 0.57 (eluent $CHCl_3/Me_2CO$, 40:1, v/v); ν_{max} (KBr)/cm^{-1} 2926 m (C−H), 1648 s (C═N); δ_H (300 MHz, $CDCl_3$) 1.08 (12H, t, *J* = 6.9 Hz, CH_3 from NEt_2), 2.18 (6H s, CH_3 from C_6H_4Me-*p*), 3.63 (8H, br s, CH_2 from NEt_2), 6.32 (4H, d, *o*-protons from C_6H_4Me-*p*), 6.73 (4H, d, *m*-protons from C_6H_4Me-*p*), 7.24 and 7.51 (20H, 2 m, $H_{aromatic}$); δ_C (75.5 MHz, CD_2Cl_2) 14.2 (CH_3 from NEt_2), 21.3 (CH_3 from C_6H_4Me-*p*), 43.6 (CH_2 from NEt_2), 98.1 (N−C−N), 122.2, 126.9, 128.6, 128.8, 132.8, 135.8, 138.2, and 141.5 ($C_{aromatic}$), 161.1 (C(O)═N).

35 (96.6 mg, 90%). Found: C, 53.53; H, 4.49; N, 7.82 (calcd for $C_{48}H_{48}N_6Cl_4O_2Pt$: C, 53.49; H, 4.49; N, 7.80); *m*/*z* (high-resolution ESI$^+$) 1114.1877 ([M + K]$^+$, requires 1114.1878); R_f = 0.61 (eluent $CHCl_3/Me_2CO$, 40/1, v/v); ν_{max} (KBr)/cm^{-1} 2924; 2852, m (C−H), 1647, s (C═N); δ_H (300 MHz, $CDCl_3$) 1.07 (12H, t, *J* = 6.9 Hz, CH_3 from NEt_2), 3.62 (8H, br s, CH_2 from NEt_2), 6.36 (4H, d, *o*-protons from C_6H_4Cl-*p*), 6.90 (4H, d, *m*-protons from C_6H_4Cl-*p*), 7.31 and 7.51 (20H, 2 m, $H_{aromatic}$); δ_C (75.5 MHz, CD_2Cl_2) 14.1 (CH_3 from NEt_2), 43.7 (CH_2 from NEt_2), 98.4 (N−C−N), 123.3, 127.1, 128.4, 131.5, 132.6, 137.8, and 142.8 ($C_{aromatic}$), 160.9 (C(O)═N).

36 (85.0 mg, 80%). Found: C, 56.16; H, 5.10; N, 7.88 (calcd for $C_{50}H_{54}N_6Cl_2O_4Pt$: C, 56.18; H, 5.09; N, 7.86); *m*/*z* (high-resolution ESI$^+$) 1090.3127 ([M + Na]$^+$, requires 1090.3129); R_f = 0.58 (eluent $CHCl_3/Me_2CO$, 40:1, v/v); ν_{max} (KBr)/cm^{-1} 2926 m (C−H), 1648 s (C═N); δ_H (300 MHz, $CDCl_3$) 1.08 (12H, t, *J* = 6.9 Hz, CH_3 from NEt_2), 3.63 (8H, br s, CH_2 from NEt_2), 3.68 (6H, s, CH_3 from *p*-$MeOC_6H_4$), 6.32 (4H, d, *o*-protons from *p*-$MeOC_6H_4$), 6.77 (4H, d, *m*-protons from *p*-$MeOC_6H_4$), 7.31 and 7.40 (20H, 2 m, $H_{aromatic}$); δ_C (75.5 MHz, CD_2Cl_2) 14.2 (CH_3 from NEt_2), 43.6 (CH_2 from NEt_2), 61.9 (CH_3 from *p*-$MeOC_6H_4$), 98.1 (N−C−N), 122.1, 126.8, 128.6, 128.7, 132.6, 136.3, 138.2, and 141.3 ($C_{aromatic}$), 161.2 (C(O)═N).

37 (78.5 mg, 76%). Found: C, 58.14; H, 4.81; N, 8.15 (calcd for $C_{50}H_{50}N_6Cl_2O_2Pt$: C, 58.14; H, 4.88; N, 8.14); *m*/*z* (high-resolution ESI$^+$) 1070.2651 ([M + K]$^+$, requires 1070.2657); R_f = 0.59 (eluent $CHCl_3/Me_2CO$, 40:1, v/v); ν_{max} (KBr)/cm^{-1} 2924 m (C−H), 1667 s (C═N); δ_H (300 MHz, $CDCl_3$) 1.50 (12H, br s, β- and γ-protons

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from NC_5H_{10}), 3.54 (8H, br s, α-protons from NC_5H_{10}), 6.41, 6.93, 7.22, and 7.46 (30H, 4 m, $H_{aromatic}$); δ_C (75.5 MHz, $CDCl_3$): 24.2 (γ-carbons from NC_5H_{10}), 26.4 (β-carbons from NC_5H_{10}), 48.7 (α-carbons from NC_5H_{10}), 98.4 (N−C−N), 121.5, 126.1, 127.2, 128.2, 129.1, 132.5, 137.8, and 144.1 ($C_{aromatic}$), 160.3 (C(O)=N).

38 (94.2 mg, 90%). Found: C, 58.90; H, 5.14; N, 7.94 (calcd for $C_{52}H_{54}N_6Cl_2O_2Pt$: C, 58.86; H, 5.13; N, 7.92); *m/z* (high-resolution ESI$^+$) 1098.2976 ([M + K]$^+$, requires 1098.2970); R_f = 0.62 (eluent $CHCl_3$/Me_2CO, 40/1, v/v); ν_{max} (KBr)/cm^{-1} 2924 m (C−H), 1667 s (C=N); δ_H (300 MHz, $CDCl_3$) 1.50 (12H, br s, β- and γ-protons from NC_5H_{10}), 2.18 (6H, s, CH_3 from C_6H_4Me-*p*), 3.54 (8H, br s, α-protons from NC_5H_{10}), 6.43 (2H, d, *o*-protons from C_6H_4Me-*p*), 6.70 (2H, d, *m*-protons from C_6H_4Me-*p*), 7.27 and 7.51 (20H, 2 m, $H_{aromatic}$); δ_C (75.5 MHz, $CDCl_3$) 21.1 (CH_3 from C_6H_4Me-*p*), 24.3 (γ-carbons from NC_5H_{10}), 26.4 (β-carbons from NC_5H_{10}), 48.8 (α-carbons from NC_5H_{10}), 98.0 (N−C−N), 122.2, 126.7, 128.6, 128.6, 132.8, 135.8, 138.1, and 141.2 ($C_{aromatic}$), 161.2 (C(O)=N).

39 (96.5 mg, 88%). Found: C, 54.55; H, 4.39; N, 7.66 (calcd for $C_{50}H_{48}N_6Cl_4O_2Pt$: C, 54.50; H, 4.35; N, 7.63); *m/z* (high-resolution ESI$^+$) 1138.1875 ([M + K]$^+$, requires 1138.1878); R_f = 0.60 (eluent $CHCl_3$/Me_2CO, 40:1, v/v); ν_{max} (KBr)/cm^{-1} 2924 m (C−H), 1667 s (C=N); δ_H (300 MHz, $CDCl_3$) 1.49 (12H, br s, β- and γ-protons from NC_5H_{10}), 3.53 (8H, br s, α-protons from NC_5H_{10}), 6.49 (4H, d, *o*-protons from C_6H_4Cl-*p*), 6.88 (4H, d, *m*-protons from C_6H_4Cl-*p*), 7.32 and 7.50 (20H, 2 m, $H_{aromatic}$); δ_C (75.5 MHz, $CDCl_3$) 24.2 (γ-carbons from NC_5H_{10}), 26.4 (β-carbons from NC_5H_{10}), 48.8 (α-carbons from NC_5H_{10}), 98.4 (N−C−N), 123.2, 127.2, 128.2, 131.3, 132.8, 137.8, and 142.9 ($C_{aromatic}$), 160.2 (C(O)=N).

40 (85.4 mg, 78%). Found: C, 57.10; H, 5.00; N, 7.74 (calcd for $C_{52}H_{54}N_6Cl_2O_4Pt$: C, 57.14; H, 4.98; N, 7.69); *m/z* (high-resolution ESI$^+$) 1130.2865 ([M + K]$^+$, requires 1130.2868); R_f = 0.60 (eluent $CHCl_3$/Me_2CO, 40:1, v/v); ν_{max} (KBr)/cm^{-1} 2924 m (C−H), 1667 s (C=N); δ_H (300 MHz, $CDCl_3$) 1.50 (12H, br s, β- and γ-protons from NC_5H_{10}), 3.54 (8H, br s, α-protons from NC_5H_{10}), 3.67 (6H, s, CH_3 from *p*-$MeOC_6H_4$), 6.43 (4H, d, *o*-protons from C_6H_4OMe-*p*), 6.71 (4H, d, *m*-protons from *p*-$MeOC_6H_4$), 7.28 and 7.53 (20H, 2 m, $H_{aromatic}$); δ_C (75.5 MHz, $CDCl_3$) 24.3 (γ-carbons from NC_5H_{10}), 26.4 (β-carbons from NC_5H_{10}), 48.8 (α-carbons from NC_5H_{10}), 61.7 (CH_3 from *p*-$MeOC_6H_4$), 98.0 (N−C−N), 122.1, 127.4, 128.6, 129.4, 132.1, 136.8, 138.8, and 141.2 ($C_{aromatic}$), 161.3 (C(O)=N).

Synthesis of ***41***. An excess of nitrone **6** (5 mmol) was added to a suspension of **2** (0.5 mmol) and **27** in $CHCl_3$ (6 mL), and the reaction mixture was stirred for 120 h at 25 °C. The solution was separated by filtration. Complex **41** was isolated from the solution by column chromatography on SiO_2 (eluent $CHCl_3$/Et_2O, 40:1.5, v/v). The solvent was evaporated *in vacuo* at 20−25 °C to give a yellow, oily residue. The residue was crystallized under *n*-hexane to form the yellow powder of **41**. The complex was dried in air at 20−25 °C. Yield: 8%.

41 (39.8 mg, 8%). Found: C, 55.70; H, 4.27; N, 5.75 (calcd for $C_{45}H_{41}N_4Cl_3O_2Pt$: C, 55.65; H, 4.25; N, 5.77); *m/z* (high-resolution ESI$^+$) 992.1841 ([M + Na]$^+$, requires 992.1841); R_f = 0.72 (eluent $CHCl_3$/Et_2O, 40:1.5, v/v); ν_{max} (KBr)/cm^{-1} 2934, 2978 m (C−H), 1643 s (C=N); δ_H (300 MHz, CDCl) 1.30 (6H, m, CH_3 from both Et of the different 2,3-dihydro-1,2,4-oxadiazole ligands), 2.14 (3H, s, CH_3 from C_6H_4Me-*p*), 2.85 (4H, q, CH_2 from Et of the different 2,3-dihydro-1,2,4-oxadiazole ligands), 6.47, 6.73, 6.82, 7.33, and 7.51 (28H, 5 m, $H_{aromatic}$); δ_C (75.5 MHz, CD_2Cl_2) 9.9 (CH_3 from Et of the different 2,3-dihydro-1,2,4-oxadiazole ligands), 21.2 (CH_3 from C_6H_4Me-*p*), 22.5 (CH_2 from Et of the different 2,3-dihydro-1,2,4-oxadiazole ligands), 98.3 (N−C−N of the different 2,3-dihydro-1,2,4-oxadiazole ligands), 122.3, 123.3, 126.5, 127.6, 128.7, 128.9, 132.5, 135.4, 137.3, 138.2, and 141.3 ($C_{aromatic}$), 161.2 (C(O)=N of the different 2,3-dihydro-1,2,4-oxadiazole ligands).

Liberation of the 2,3-Dihydro-1,2,4-oxadiazoles from ***26*** *and* ***30***. An excess of NaCN (10 mg, 0.2 mmol) in methanol-d_4 (0.5 mL) was added to a suspension of either of **26** or **30** (0.025 mmol) in $CDCl_3$ (0.1 mL), and the reaction mixture was stirred for 3 d at 35 °C. During this time, the initially pale yellow suspension turned to a colorless solution. Completeness of the reaction was monitored by ^{1}H NMR and high-resolution ESI-MS, indicating that the conversion is complete after 3 d. The metal-free heterocycles were separated from excess NaCN, and also from NaCl and $Na_2[Pt(CN)_4]$, formed in the reaction, by evaporation of the solvent at room temperature and treating the colorless, oily residue with $CHCl_3$. The liquid phase was separated by filtration, whereupon evaporation of the solvent afforded in almost quantitative yields **42** and **43** as colorless, oily residues.

42. *m/z* (high-resolution ESI$^+$) 365.1626 ([M + Na]$^+$, requires 365.1629); δ_H (300 MHz, $CDCl_3$) 1.27 (6H, t, *J* = 7.6 Hz, CH_3 from Et), 2.14 (6H, s, CH_3 from C_6H_4Me-*p*), 2.75 (4H, q, *J* = 7.6 Hz, CH_2 from Et), 6.45 (4H, d, *o*-protons from C_6H_4Me-*p*), 6.71 (4H, d, *m*-protons from C_6H_4Me-*p*), 7.24 and 7.51 (20H, 2 m, $H_{aromatic}$); δ_C (75.5 MHz, CD_2Cl_2) 9.9 (CH_3 from Et), 21.2 (CH_3 from C_6H_4Me-*p*), 22.3 (CH_2 from Et), 96.3 (N−C−N), 122.2, 126.7, 128.6, 128.7, 132.8, 134.9, 138.1, and 141.2 ($C_{aromatic}$), 162.0 (C(O)=N).

43. *m/z* (high-resolution ESI$^+$) 380.1731 ([M + Na]$^+$, requires 380.1739); δ_H (300 MHz, CD_2Cl_2) 2.20 (3H, s, CH_3 from C_6H_4Me-*p*), 2.97 (12H, br s, NMe_2), 6.30 (4H, d, *o*-protons from C_6H_4Me-*p*), 6.77 (4H, d, *m*-protons from C_6H_4Me-*p*), 7.25 and 7.42 (20H, 2 m, $H_{aromatic}$); δ_C (75.5 MHz, $CDCl_3$) 21.3 (CH_3 from C_6H_4Me-*p*), 39.3 (NMe_2), 97.5 (N−C−N), 122.1, 126.4, 128.3, 128.8, 131.9, 135.9, 137.9, and 141.6 ($C_{aromatic}$), 161.2 (C(O)=N).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Full tables of crystal data, atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, and bond lengths and angles for **25** and **33** as CIF files. Discussion of the theoretical results on DCA to methylenecyclopropane; table with calculated energies. Characterization of nitrones **6**−**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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