Synthesis and characterization of novel olefin complexes of palladium(0) with chelating bis(N-heterocyclic carbenes) as spectator ligands

T. Scattolina, L. Canoveseb,⇑ F. Visentina, C. Santoa, N. Demitrib

a Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca’ Foscari, Venice, Italy
b Elettra – Sincrotrone Trieste, S S 14 Km 163 5 in Area Science Park, 34149 Basovizza, Trieste, Italy

ABSTRACT

We have synthesized several novel palladium(0) olefin complexes stabilized by strong σ-donating bis-chelating carbene ligands characterized by one or two CH2 spacers and electron-withdrawing olefins. Although it appears obvious that the σ-donating carbenes and electron-withdrawing olefins should cooperate in the stabilization of the ensuing complexes, the limit of their coexistence was not hitherto clear. On the basis of previously measured stabilizing capability of the olefins toward Pd(0) complexes we were able to synthesize ten complexes (nine new and one synthesized by a different protocol from that of the literature). The less electron-withdrawing olefin capable of stabilizing the complex was dimethylfumarate. However, the most interesting results were obtained with the (Z)-1,2-bis(p-tolylsulfonyl)ethene (cis-sulf) which instantly isomerizes upon coordination and in the case of the derivative bearing the olefin tetramethyl ethene-1,1,2,2-tetracarboxylate (tmetc) whose decomposition in CD2Cl2 yields the saturated tetramethyl ethane-1,1,2,2-tetracarboxylate (D2). The solid-state structure of the complex 4d bearing the bis-carbene 1,10-dibenzyl-3,30-methylenediimidazol-2,20-diyldiene and the olefin (E)-1,2-bis(p-tolylsulfonyl)ethene (trans-sulf) was also determined.

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1. Introduction

The stability and performance of homogeneous catalysts throughout the turnover processes is strongly influenced by the nature of the ligands and metal. In this respect thanks to its redox potentials which allow an easy shift between two quite stable oxidation states, Pd(II) and Pd(0) catalysts or pro-catalysts [1] have been very frequently studied and used mainly in the field of the homo- and hetero-cross coupling [2].

Beside the widespread use of phosphines as stabilizing ligands, most recently, NHC ligands have become quite popular in the preparation of stable palladium catalysts [3] owing to their intrinsic stability toward heat, moisture and air and their low toxicity [4].

As a matter of fact, their strong donating capability can compete with other commonly used ligands in the stabilization of their complexes whereas the steric hindrance of the NHC can be easily tuned-up by an accurate choice of the substituents at the imidazolic nitrogen [5], as was at once apparent after the synthesis of the first stable NHC derivatives [6].

In particular, since the 90s bis-carbene palladium complexes have been widely investigated and many catalysts displaying remarkable enantioselectivity synthesized [7].

However, the σ-donor NHC ligands, strongly conflict with the electron density of the olefin stabilized d10 complexes and therefore very few species of this type are described in the literature [8]. Among them, only few Pd(0) olefin complexes bearing chelating bis-carbenes as spectator ligands, stabilized by the strongly withdrawing maleic anhydride were synthesized by Elsevier and co-workers [9].

We have been involved in studies dealing with the synthesis and reactivity of Pd(0) olefin complexes for many years. In particular, we were able to correlate the mutual stability imparted by the olefin to Pd(0) and Pt(0) complexes stabilized by homogeneous spectator ligands and eventually summarize the general trend that is reported in Scheme 1 [10].

\[
[(L - L’)pd(\eta^2 – olefin_1)] + olefin_2 \Rightarrow [(L - L’)pd(\eta^2 – olefin_2)] + olefin_1
\]

It was therefore interesting for us to try and synthesize chelating NHC Pd(0) olefin complexes and establish which olefin of the cited ones could be coupled with the strong σ-character of the bis-carbene ligand. In this respect we have successfully
2. Results and discussion

2.1. General remarks

The complexes 1a–c [11], 1d–d’ [12], 1e [13] and the imidazolium salts [7c] were synthesized according to published procedures. The silver carbene complexes 2, 3 were obtained by adding in the dark Ag2O in slight stoichiometric excess to a methanol solution of the corresponding imidazolium salt [14]. The reaction progress was monitored by the progressive disappearance of the solid Ag2O, whereas the 1H and 13C NMR spectra of the isolated derivatives and in particular the disappearance of the signal ascribable to the imidazolium proton within 9–10 ppm confirm the formation of the expected species (See Fig. S1, Supplementary Material). Derivatives 1a–e and 1f were chosen as starting complexes thanks to their remarkable stability coupled with the peculiar reactivity which make easy the displacement of the spectator ligands in many exchange reactions [15]. The trans-metalation reaction between complexes of type 1 and silver carbenes yields the palladium carbene olefin derivatives according to Scheme 3.

The type 4 and 5 complexes were characterized by elemental analysis, IR, 1H and 13C NMR spectrometry. In the case of complex 4d the solid state structure was also determined by X-ray diffractometry.

2.2. Maleic anhydride and fumaronitrile complexes 4a–4b and 5a–5b

The complexes of type 4 and 5 were obtained by reacting in CH2Cl2 the starting complexes 1a or 1b with the silver derivatives 2 or 3 according to the protocol reported in Scheme 3. The complexes 4a–b and 5a–b were all synthesized under similar experimental conditions (RT, reaction time: 30’). Although the synthesis of complex 4a was already published we have chosen

Scheme 1. Stability rank imparted to Pd(0) complexes by the deactivated olefins based on the equilibrium constant of the reaction.

Scheme 2. Starting ligands, silver intermediates and Pd(0) olefin bis-carbene complexes.
to follow our synthetic approach which in this case gave similar selectivity and yield than those previously proposed by Elsevier and co-workers [9]. Moreover, it is worth noting that the versatility of our protocol summarized in Scheme 3 was exploited in the synthesis of all the other complexes reported in this paper. Thus complexes 4b and 5a, b were separated from the reaction mixture and characterized.

The relevant spectra of complexes 4a, b and 5a–b are reported in Supplementary Material Figs. S2a–c and S3a–c and the complete NMR characterization in the Section 5.

In particular, the $^1$H NMR spectra of the maleic anhydride (ma) derivatives 4a and 5a are comparable and characterized by one singlet at ca. 3.6–3.7 ppm due to the olefin protons of ma, two doublets at ca. 6.9–7.2 ppm due to imidazole protons, one AB system at 5.3–5.4 ppm of methylenic protons of the imidazole benzyl substituents and finally one AB system at ca. 5.9 ppm or one multiplet at ca. 4.7 ppm ascribable to the protons of the spacers of complex 4a or 5a, respectively. The $^{13}$C NMR spectra display the signal of carbene carbon at ca. 184–186 ppm, the carbonyl carbon at ca. 175 ppm and the olefin carbon at ca. 39 ppm. The benzyl $\text{CH}_2$ resonates at ca. 55 and 65 ppm whereas the carbons of the spacers at 50 or 49 ppm in the case of 4a or 5a, respectively.

As for the $^1$H NMR characterization of fumaronitrile (fn) derivatives 4b and 5b which not surprisingly again display comparable spectra, the most relevant signals are a singlet at ca. 2.3–2.5 ppm related to the olefin protons, a couple of doublets within 6.8 and 7.2 ppm of the imidazole protons, one AB system for the methylene $\text{CH}_2$–Ph protons. The presence of a singlet at ca. 6 ppm in the case of complex 4b (spacer $\text{N}−\text{CH}_2−\text{N}$) and of one AB system within 4.6–5.0 ppm for the complex 5b (spacer $\text{N}−\text{CH}_2−\text{N}$) completes the assignment of the protons.

The $^{13}$C NMR spectra exhibit the signals ascribable to carbon of the coordinated carbene, of the nitrile (CN) and of the benzyl ($−\text{CH}_2−\text{Ph}$) groups at ca. 186, 127, and 55 ppm, respectively. The signals related to the olefin at ca. 13 ppm, those at 63 (4b) and at 49 ppm (5b) ascribable to the carbons of the spacers and those of the imidazole carbons within 119–122 ppm, complete the NMR characterization.

2.3. Naphthoquinone complex 4c

Owing to the instability in solution of the naphthoquinone (nq) derivatives following the protocol of Scheme 3 we were able to synthesize at 223 K and characterize at 243 K only complex 4c.

As can be deduced from the $^1$H and $^{13}$C NMR spectra of complex 4c reported in Supplementary Material (Fig. S4a–b) the olefin protons resonate at ca. 5.0 ppm, whereas at 5.2–5.8 ppm the AB system related to the CH$_2$–Ph protons can be traced back. The singlet at ca. 5.6 ppm and a couple of doublets within 6.8–7 ppm ascribable to the N−CH$_2$−N and to the imidazole protons together with the aromatic signals within 7.2 and 8 ppm are identified in the $^1$H NMR spectrum. The $^{13}$C NMR spectrum of 4c displays the resonances of carbene and carbonyl carbons at ca. 182 and 178 ppm, respectively. The benzyl, the olefin and the carbons of the spacer resonate at ca. 53, 63 and 62 ppm, respectively (See Supplementary Material Fig. S3a–c and Section 5).

2.4. (E)-1,2-bis(p-tolylsulfonyl)ethene complexes 4d and 5d

(E)-1,2-bis(p-tolylsulfonyl)ethene (trans-sulf) was obtained following published procedures [16] and is the most stabilizing olefin among those used in this work. As a matter of fact complexes 4d or 5d were promptly obtained on following the usual protocol of Scheme 3 starting from complex 1d and the silver derivatives 2 or 3. However, the synthesis of the analogous complexes bearing the olefin (Z)-1,2-bis(p-tolylsulfonyl)ethene (cis-sulf) 4d and 5d starting from 1d, failed. Independently of the starting complexes 1d or 1d we obtained in any case complexes 4d and 5d bearing the trans-sulf as stabilizing olefin (See Scheme 4). The isolated complexes are stable and were characterized by NMR and IR techniques (See Supplementary Material Fig. S5a–d and Section 5). Thus, in the $^1$H NMR spectra of both the complexes it is possible to observe a singlet (CH$_2$ protons of the tolyl groups of the olefin) at 2.4 ppm, a singlet at ca. 3.7–3.8 ppm (olefinic protons), a singlet at 5.8 ppm (spacer of 4d), an AB system within 4.6–5 ppm (spacer of 5d) and eventually an AB system within 5.3–5.8 ppm (CH$_2$ protons of the benzyl substituents). The $^{13}$C
NMR spectra are characterized by a signal at ca. 21–22 ppm (C<sub>H</sub><sub>3</sub>-Tol), a couple of peaks at 55 and 56 ppm (olefin carbons and benzyl CH<sub>2</sub>, respectively), the spacer carbons at 63 (NCH<sub>2</sub>H) and 48.7 ppm (NCH<sub>2</sub>CH<sub>2</sub>N) and finally the coordinated carbene carbon at ca. 186 ppm.

The solid-state structure of complex 4d was determined and its ORTEP representation [17] is reported in Fig. 1 whereas the discussion will be dealt later.

The isomerization of the coordinated olefins to the Pd(0) center, although not unprecedented, was faster in this case with the bis-carbene as spectator ligand than that we have previously observed when the ancillary ligands were chelating phosphoquinolines [12]. As a matter of fact, at variance with the reaction rate which was hitherto measureable by NMR technique, in the present case the rate of formation of complex 4d (or 5d) starting from 1d was not measured, the olefin isomerization being almost immediate (few minutes). Thus, the NMR spectra can only reveal the appearance of the final species 4d (or 5d). Apparently, the strong σ-donating character of the Fischer bis-carbene promotes the olefin isomerisation much more efficiently than phosphine ligands.

In particular, according to the mechanism proposed [12] we surmise that the enhanced electronic density on palladium promoted by the bis-carbene favors the formation of the intermediate reported in Scheme 5.

2.5. Tetramethyl ethene-1,1,2,2-tetracarboxylate complex 4e

The occurrence of the trans-metalation between 1e and complexes 2, 3 was observed in both cases by <sup>1</sup>H NMR spectroscopy, but only complex 4e was stable enough to be isolated and characterized.

In order to minimize the decomposition of complex 4e, the trans-metalation was carried out at 223 K and the ensuing complex isolated by customary methods (See Section 5). The <sup>1</sup>H NMR spectrum of complex 4e displays the singlet at 3.5 ppm (OCH<sub>3</sub> groups) and those at 5.6 and 5.8 ppm were assigned to CH<sub>2</sub>Ph and NCH<sub>2</sub>N protons, respectively (Fig. S6a Supplementary Material). The <sup>13</sup>C NMR spectrum displays the carbenic and carbonyl signals at 188 and 168 ppm, whereas the carbons of the OCH<sub>3</sub>, CH<sub>2</sub>Ph and NCH<sub>2</sub>N resonate at 51, 54 and 64 ppm, respectively (Fig. S6b Supplementary Material).

A quite intriguing peculiarity related to complex 4e emerged as a consequence of its 24 h decomposition in CD<sub>2</sub>Cl<sub>2</sub> or CDCl<sub>3</sub> solution. Beside the solid products of decomposition a novel species characterized by a very simple <sup>1</sup>H NMR spectrum was detected in the filtered solution (Fig. 2).

In order to understand the nature of the species we have performed the mass spectrometry of the compound which was identified as tetramethyl ethane-1,1,2,2-tetracarboxylate (D<sub>2</sub>). As a matter of fact similar species were proposed by Spencer and co-workers in the case of palladium catalyzed reduction of cis-olefins [18] but we cannot exclude a mechanism involving radicals for the decomposition process. Eventually, we have carried out the decomposition in CH<sub>2</sub>Cl<sub>2</sub> and as can be seen in the mass spectrum of Fig. 3, we obtained the undeuterated analog tetramethyl ethane-1,1,2,2-tetracarboxylate.

2.6. Dimethylfumarate complexes 4f and 5f

Since it is not possible to prepare the pure dimethylfumarate derivative of the 2-methyl-6-(phenylthiomethyl)pyridine ligand, complexes 4f and 5f were synthesized starting from complex 1f.
which is stabilized by the spectator ligand 2-methyl-8-(methylthio)quinoline (See Scheme 2). It was already stated that complexes characterized by the concomitant coordination of a strong σ-donor carbene (two in this case) need a strongly deactivated olefin to be stabilized. Yet, dimethylfumarate (dmfu), among the investigated olefins, is the less performing one. However, we were able to synthesize (at 233 K), isolate and characterize by usual spectral techniques the complexes 4f and 5f. Thus, (see Fig. S7a–d, Supplementary Material) the 1H NMR spectra of both derivatives display two singlets at ca. 3.3 and 3.6 ppm ascribable to OC\textsubscript{3}H\textsubscript{3} and olefin protons, respectively. Another singlet at 5.3 (or 5.9) ppm related to the proton of the spacers NC\textsubscript{2}H\textsubscript{2}N (or NC\textsubscript{2}H\textsubscript{2}C\textsubscript{2}H\textsubscript{2}N), an AB system within 4.6–5.6 ppm (C\textsubscript{2}H\textsubscript{2}Ph) and a doublet within 6.8–7.2 ppm (imidazole protons) are found in the proton spectra. In the 13C NMR spectra the signals at 38 (olefin carbons), 51 (O\textsubscript{C}H\textsubscript{3}), 53 (C\textsubscript{H}Ph) and within 55–53 ppm (NC\textsubscript{2}H\textsubscript{2}N and NC\textsubscript{2}H\textsubscript{2}C\textsubscript{2}H\textsubscript{2}N spacers, respectively) are detected. The complete assignment of the signals is given by those at ca. 178 ppm (C\textsubscript{O}) and at ca. 187 ppm (coordinated carbene carbon).

3. X-ray diffraction analysis

3.1. Structural characterization of complex 4d

The crystalline form of 4d contains one crystallographically independent palladium complex (Figs. 1 and S8a–b in Supplementary Material). A query on CSD (version 5.39), using the Olefin-Pd-1,1\textsubscript{0}0-1,1\textsubscript{0}0-methylenediimidazol-2,2\textsubscript{0}0-diylidene fragment gives, as a result, the structure of a similar Pd(0) complex bound to an imidazolylidene ligand and maleic anhydride (CCDC 908658) [9a]. The palladium(0) centre in this complex adopts a square planar coordination sphere, equivalent to 4d, with similar bond lengths and angles (Tables 1 and S1; Supplementary Material). Table S1 shows that the low oxidation state leads to significantly longer bond lengths compared to similar Pd(II) complexes [19] (or Rh(III) [20]), bearing the same imidazolylidene ligand used in this work.

The 1,1\textsubscript{0}0-dibenzyl-3,3\textsubscript{0}0-methylenediimidazol-2,2\textsubscript{0}0-diylidene scaffold is rather flexible as shown by the angle between the imidazole average planes. Similar values have been found among A and the two square planar Pd(II) complexes reported in Table S1 (see line “Imidazole Ave. Planes”) but they are significantly reduced (33.77° /C\textsubscript{176}6) in the Rh complex [C] (CCDC number 633257) which bears the same ligand reported in this work, in a bulkier octahedral coordination sphere (Fig. S9a; Supplementary Material).

The C=C double bond of the olefin, which is π\textsuperscript{2} coordinated to the metal center and almost perpendicular to the coordination plane, is lengthened compared to the free alkene due to π-back bonding from the Palladium(0).

Crystal packing of 4d shows hydrophobic contacts among neighbor molecules, involving CH⋯π and π⋯π interactions. Furthermore, 4d structure shows intramolecular stacking between the tosyl groups of the coordinated olefin (Fig. S9b: Supplementary Material – angle between phenyl mean planes is 1.83(1)/C\textsubscript{176}, with average distance between planes of 3.66(1) Å and 1.36 Å ring centroids slippage).

4. Conclusion

We have synthesized ten new Pd(0) complexes with six different deactivated olefins bearing bulky bis-carbenes as spectator ligands. Thanks to our synthetic protocol based on the trans-metallation reaction between silver carbene and Pd(0) olefin pyridylthioether (or quinolylthioether) complexes we have isolated quite elusive species otherwise not easily achievable. The isolated species stabilized by maleic anhydride, fumaronitrile and 1,2-bis(p-tolylsulfonyl)ethene were stable in the solid and in solution. The

![Fig. 3. Mass spectra of tetramethyl ethane-1,1,2,2-tetracarboxylate (top) and tetramethyl ethane-1,1,2,2-tetracarboxylate (D2) (bottom).](image-url)
derivatives of dimethylfumarate and naphthoquinone decompose in solution giving undefined products, whereas the tetramethylhexa-1,1,2,2-tetracarboxylate complexes decompose yielding unexpectedly the tetramethylhexa-1,1,2,2-tetracarboxylate (D₂). Generally speaking, the synthesized species fits in the stability trend imparted by olefins we established so far [10]. Moreover, the presence of the bis-carbene ligand promotes a faster isomerization of the olefin (Z)-1,2-bis(p-tolylsulfonyl)ethene (cis-sulf) into (E)-1,2-bis(tolylsulfonyl)ethene (trans-sulf) than that previously observed [12]. Finally one of the few available solid-state structures of this kind of derivatives was resolved.

5. Experimental

5.1. Solvents and reagents

The solvent CH₂Cl₂ and CHCl₃ were distilled over CaH₂, acetone was refluxed over 4 Å molecular sieves and distilled. All other solvents and chemicals were commercial grade products and used as purchased.

5.2. IR, NMR, UV–Vis measurements and elemental analysis

The IR, ¹H, ¹³C and ³¹P NMR spectra were recorded on a Perkin-Elmer Spectrum One spectrophotometer and on a Bruker 300 Avance spectrometer, respectively. The elemental analysis of the synthesized complexes was carried out using an Elementar CHN “CUBO micro Vario” analyzer.

5.3. Crystal structure determination

The crystal data of 4d were collected at 100 K at the XRD1 beamline of the Elettra Synchrotron, Trieste (Italy) [21], using a monochromatic wavelength of 0.700 Å. The data sets were integrated and corrected for Lorentz and polarization effects with the XDS package [22]. Semi-empirical absorption corrections and scaling were performed on datasets, exploiting multiple measurements of symmetry-related reflections, using SADABS program [23].

5.4. Synthesis of the silver complexes 2 and 3

To 269.3 mg (0.543 mmol) of the imidazolium salt 1,1′-dibenzyl-3,3′-methyleneidimiazolium dibromide ([BnImCH₂CH₂ ImBn]H₂Br₂) dissolved in 35 ml of anhydrous methanol in a two neck 100 ml flask, under inert atmosphere (Ar) 165.5 mg (0.714 mmol) of Ag₂O, were added. The resulting mixture was stirred in the dark for 2 h and then filtered off on a millipore apparatus. The clear solution was dried under vacuum, dissolved in the minimum volume of CH₂Cl₂ and the title complex precipitated by addition of diethyl ether as a pink solid. The product was filtered off in a gouch flask, under inert atmosphere (Ar) 55.4 mg (yield 95%) of the title compound were obtained as a brown solid.

6. Synthesis of type 4 complexes

6.1. Synthesis of the ma complex 4a

To 45.8 mg (0.110 mmol) of complex 1a dissolved in 20 ml of anhydrous CH₂Cl₂ in a two neck 50 ml flask under inert atmosphere (Ar) 76.8 mg (0.110 mmol) of the silver complex 2a was obtained (yield 59%).

6.2. Synthesis of the ma complex 5a

Brown microcrystals, 20 min, yield 99%.

6.3. IR, NMR, UV–Vis measurements and elemental analysis

The IR, ¹H, ¹³C and ³¹P NMR spectra were recorded on a Perkin-Elmer Spectrum One spectrophotometer and on a Bruker 300 Avance spectrometer, respectively. The elemental analysis of the synthesized complexes was carried out using an Elementar CHN “CUBO micro Vario” analyzer.
6.3. Synthesis of the fn complex 4b

Brown microcrystals, 30 min, yield 97%.

\(^{1}{H}\) NMR (300 MHz, CDCl\(_3\), \(T = 298\) K, ppm) \(\delta\): 2.52 (s, 2H, 2CH\(_3\)), 4.63–4.90 (AB system, 4H, \(J = 14.6\) Hz, 2CH\(_2\)Ph), 5.97 (s, 2H, NCH\(_3\)N), 6.95 (d, 2H, \(J = 1.9\) Hz, 2CH\(_3\)im), 7.17 (d, 2H, \(J = 1.9\) Hz, 2CH\(_3\)im), 7.29–7.39 (m, 18H, aryl-H).

\(^{13}{C}\)\(^{1}{H}\) NMR (CDCl\(_3\), \(T = 298\) K, ppm) \(\delta\): 21.5 (CH\(_3\), CH\(_2\)), 54.6 (CH\(_2\)), 55.9 (CH\(_2\), CH=Ph), 63.1 (CH\(_2\), NCH\(_3\)N), 119.6 (CH, CH\(_3\)), 120.8 (CH, CH\(_3\)), 126.1–141.4 (Ph), 185.8 (C, carbene).

Anal. Calc. for C\(_{27}\)H\(_{18}\)N\(_4\)O\(_4\)Pd: C, 56.87; H, 4.95; N, 9.29.

IR (KBr): \(\nu = 1660\) cm\(^{-1}\), \(\nu_{C=O} = 1237\) cm\(^{-1}\).

6.8. Synthesis of the ng complex 4c

To 24.5 mg (0.05 mmol) of complex 1a dissolved in 30 mL of anhydrous CH\(_2\)Cl\(_2\) in a two neck 100 mL flask under inert atmosphere (Ar) at 223 K (ethanol/liquid N\(_2\)). 32.6 mg (0.046 mmol) of the silver complex were obtained as a brown solid.

\(^{1}{H}\) NMR (300 MHz, CDCl\(_3\), \(T = 298\) K, ppm) \(\delta\): 4.77 (s, 2H, 2CH\(_3\)im), 5.28–5.66 (AB system, 4H, \(J = 15.0\) Hz, 2CH\(_2\)Ph), 5.70 (s, 2H, NCH\(_3\)N), 6.88 (d, 2H, \(J = 1.9\) Hz, 2CH\(_3\)im), 7.07 (d, 2H, \(J = 1.9\) Hz, 2CH\(_3\)im), 7.25–7.93 (m, 14H, aryl-H).

\(^{13}{C}\)\(^{1}{H}\) NMR (CDCl\(_3\), \(T = 298\) K, ppm) \(\delta\): 54.1 (CH\(_2\), CH=Ph), 63.0 (CH\(_2\), NCH\(_3\)N), 120.5 (CH, CH\(_3\)im), 121.1 (CH, CH\(_3\)im), 124.9–138.9 (Ph), 180.5 (C, C=O), 181.4 (C, carbene).


IR (KBr): \(\nu = 1600\), 1559, 1683 cm\(^{-1}\).

Derivatives 4e and 4f were prepared in a similar way using the appropriate reagents.

The color of the complexes, the reaction time and the yield are reported at the top of each characterization.

6.9. Synthesis of the tmeq complex 4e

Brown microcrystals, 60 min, yield 65%.

\(^{1}{H}\) NMR (300 MHz, CDCl\(_3\), \(T = 298\) K, ppm) \(\delta\): 3.50 (s, 12H, 4OCH\(_3\)), 5.60 (s, 4H, 2CH\(_2\)Ph), 5.84 (s, 2H, NCH\(_3\)N), 6.80 (bd, 2H, \(J = 14.6\) Hz, 2CH\(_2\)Ph), 6.72 (bd, 2H, \(J = 14.6\) Hz, 2CH\(_2\)Ph), 7.25–7.37 (m, 10H, 2Ph). 13\(^{C}\)\(^{1}{H}\) NMR (CDCl\(_3\), \(T = 243\) K, ppm) \(\delta\): 50.9 (CH\(_2\), OCH\(_3\)), 53.8 (CH\(_2\), CH=Ph), 62.9 (CH\(_2\), NCH\(_3\)N), 120.0 (CH, CH\(_3\)im), 120.6 (CH, CH\(_3\)im), 128.4–136.1 (Ph), 167.8 (COCOCH\(_3\)), 181.4 (C, carbene).

Anal. Calc. for C\(_{31}\)H\(_{26}\)N\(_4\)O\(_2\)Pd: C, 53.57; H, 4.64; N, 8.06. Found: C, 53.72; H, 4.67; N, 7.94.

IR (KBr): \(\nu = 1712\), 1666 cm\(^{-1}\), \(\nu_{C=O} = 1239\) cm\(^{-1}\).

6.10. Synthesis of the dmfu complex 4f

Brown microcrystals, 60 min, yield 64%.

\(^{1}{H}\) NMR (300 MHz, CDCl\(_3\), \(T = 298\) K, ppm) \(\delta\): 3.31 (s, 6H, 2OCH\(_3\)), 3.56 (s, 2H, 2CH\(_3\)im), 5.36–5.53 (AB system, 4H, \(J = 14.5\) Hz, 2CH\(_2\)Ph), 5.91 (s, 2H, NCH\(_3\)N), 6.90 (d, 2H, \(J = 1.6\) Hz, 2CH\(_3\)im), 7.10 (d, 2H, \(J = 1.6\) Hz, 2CH\(_3\)im), 7.33–7.43 (m, 10H, 2Ph).

\(^{13}{C}\)\(^{1}{H}\) NMR (CDCl\(_3\), \(T = 243\) K, ppm) \(\delta\): 38.7 (CH, CH\(_3\)im), 50.4 (CH\(_2\), OCH\(_3\)), 55.3 (CH\(_2\), CH=Ph), 63.3 (CH\(_2\), NCH\(_3\)N), 119.2 (CH, CH\(_3\)im), 121.2 (CH, CH\(_3\)im), 128.0–137.3 (Ph), 176.9 (C, C=O), 187.4 (C, carbene).

Anal. Calc. for C\(_{30}\)H\(_{28}\)N\(_4\)O\(_2\)Pd: C, 56.01; H, 4.87; N, 9.68. Found: C, 56.17; H, 5.02; N, 9.53.

IR (KBr): \(\nu = 1712\), 1666 cm\(^{-1}\), \(\nu_{C=O} = 1239\) cm\(^{-1}\).