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Metal Vapor Synthesis as a Straightforward Route to Group 10 Homoleptic Carbene Complexes

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The co-condensation of nickel, palladium, or platinum vapor with the *N*,*N′*-di-*tert*-butyl heterocyclic carbene 1,3-di-*N*-*tert*-butylimidazol-2-ylidene [C{N(Bu^t)CH}$_2$] (L) provides a novel and straightforward synthesis of the stable, two-coordinate homoleptic metal carbene complexes NiL$_2$ (**1**), PdL$_2$ (**2**), and PtL$_2$ (**3**). A single-crystal X-ray structural determination of **2** and **3** shows the two complexes to be isomorphous; in the solid state the metal center is linear and two-coordinate and the molecules approach D_{2d} symmetry with a dihedral angle of 90° between the planar rings of the two ligand heterocycles. The metal center in **2** appears to be an essential mediator in the quantitative conversion of the ligated carbene into dihydroimidazoline, which is cleanly eliminated from a solution of the complex under an atmosphere of dihydrogen; **2** also reversibly coordinates ethene.

Introduction

The range of N-substituted heterocyclic carbenes containing a stable divalent carbon center has expanded considerably in recent years, as has the number and variety of transition metal complexes containing these ligated carbenes.[1−9] The latter exhibit enhanced Lewis basicity and negligible π back-bonding in comparison with tertiary phosphines and are also considered to exhibit higher metal−ligand bond strengths.[10] They are potentially sterically and electronically tunable, but chemically inert like conventional phosphines, with the additional advantage of an increased stability toward dissociation, degradative cleavage, and orthometalation reactions.[11] Thus, where metal phosphine complexes have been used as catalysts for a number of transformations in the past, interest is now turning to employment of these carbenes as ancillary ligands.[12] In this context, considerable attention has been focused on carbene complexes of the platinum group metals,[12,13] and palladium(II) carbene complexes, e.g., the bidentate carbene palladium(II) complex [Pd(I)$_2$(C{NMeCMe}$_2$)$_2$],[14] in particular have proven very successful for Heck and related C−C coupling reactions;[12,15,16] dicationic bis(carbene) palladium complexes have also been found to be effective catalysts in CO/C$_2$H$_4$ copolymerization.[17] By analogy with the conventional palladium−phosphine systems,[18,19] the unsaturated 14-electron bis(carbene)-Pd(0) species is most likely to be the active catalyst in Heck catalysis by Pd(II) bis(carbene) complexes. However, while bis(*N*,*N′*-dimesitylimidazol-2-ylidene)nickel(0) and -platinum(0) have been prepared by conventional methods and fully characterized,[7] the presumed palladium analogue has been generated only in situ,[15] and the isolation of such a species would clearly be of considerable interest in this context. We envisaged the metal atom route to be a viable method for the direct synthesis of low-coordinate metal−carbene complexes in the absence of competing ligands and herein report the application of this technique to the preparation of homoleptic carbene complexes of all three group 10 elements.

Results and Discussion

Selection of the Carbene Ligand L. The range of thermally stable carbenes that have been prepared to date exhibit a wide variety of physical properties according to the extent of alkyl substitution. The symmetrical *N*-*tert*-butyl-substituted derivative 1,3-di-*tert*-

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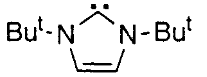
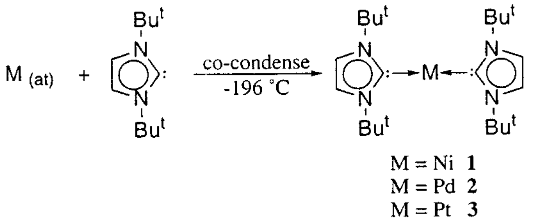


Figure 1. *N*,*N*′-di-*tert*-butylimidazol-2-ylidene, L.

butylimidazol-2-ylidene (L), shown in Figure 1, was deemed ideal for co-condensation experiments in our metal vapor synthesis (MVS) apparatus. It may be readily synthesized in 61% overall yield on a scale suitable for MVS requirements and has a high vapor pressure at low temperatures (the solid sublimes at 40 °C, 10^{-3} mbar). This allows both relatively easy introduction of the ligand vapor into the machine and removal of excess unreacted ligand from the crude product, undamaged, in up to 60% recovery. The *tert*-butyl substituents were anticipated to impart sufficient kinetic stabilization on a low-coordinate metal complex without necessarily shutting down further reaction chemistry.

Co-condensation Reactions between the Vapors of Ni, Pd, or Pt and L. Co-condensation of nickel vapor with an excess of L afforded, after workup, a brown microcrystalline, a highly air- and moisture-sensitive solid characterized as [Ni(C{N(Bu^t)CH}$_2$)$_2$], **1**, in 10% yield (eq 1). In a similar manner, the co-condensation between L and palladium or platinum vapor gave pale yellow crystalline [Pd(C{N(Bu^t)CH}$_2$)$_2$], **2**, and yellow crystalline [Pt(C{N(Bu^t)CH}$_2$)$_2$], **3**, in 32% and 25% yields, respectively. In each case only one ligand-containing product was recovered from the reaction mixture. The latter two complexes are comparatively air stable; crystals of either decompose only after a few minutes exposure to damp air.



(1)

Complexes **2** and **3** can be cleanly sublimed at 140 °C/10^{-5} mbar with around 95% recovery, but the complex **1** is unstable toward sublimation and decomposes at 80 °C at a pressure of 10^{-5} mbar. All three complexes exhibited a parent ion peak in the EI mass spectrum, but the intensity of this peak is significantly lower for **1** (at 418 amu (M$^+$)) than **2** and **3**. No peaks above 466 amu or above 555 amu were observed in the spectra of crude samples of **2** or **3,** respectively, as obtained initially from the co-condensation vessel.

While the *N*-mesityl analogues are known,[7] previous attempts to generate **1** and **3** by solution techniques have been unsuccessful to date.[20] As discussed earlier, zerovalent palladium carbene complexes are implicated in Heck catalysis, but none have been previously isolated;[15] only a few other examples of zerovalent nickel carbene complexes can be found in the literature, exemplified by [Ni{C(NMeCH$_2$)$_2$}(CO)$_3$][21] and [Ni{C(Ph)-(NBu^{t}Me)}(CH$_2$CH$_2$)$_2$].[22]

All three complexes are diamagnetic and exhibit straightforward ^{1}H and ^{13}C{^{1}H} NMR spectra (Table 1). There is only minimal change in the measured chemical shifts of the ligand protons upon complexation. It has been suggested that the NMR chemical shifts of the backbone protons are extremely sensitive to altered electron density at the atoms around the imidazole ring.[7,23,24] However, the shift to lower frequency incurred by these protons in **1**, **2,** and **3** is only significant for the nickel complex, which may indicate a degree of back-bonding from the metal in the latter. The resonance of the *tert* -butyl group protons is in each case shifted to higher frequency upon complexation, which may be attributed to the resultant changes in nitrogen p-electron density. However, we also note that the results from density functional theory calculations on the uncomplexed carbene L imply a substantial radial extension of the Cσ−1p lone pair molecular orbital at the carbenoid carbon toward the *tert*-butyl groups.[25] Thus the −CMe$_3$ protons experience considerable shielding from the lone pair at carbon in the free ligand, which may be relieved upon complexation, and hence also account for the direction of the observed shifts.

The only resonance in the ^{13}C{^{1}H} NMR spectrum that is substantially shifted upon metal complexation is that of the carbenoid carbon, from 212 to 192 ppm for **1** and to 194 ppm for **2** and **3**. This shift to lower frequency, usually of approximately 20 ppm, appears to be characteristic of metal complexes of the form M(carbene)$_2$ and presumably arises from the shielding effect of the adjacent metal center; in the *N*-mesityl analogues of **1** and **3** the values of δ for the carbenoid carbon are 193.2 and 197.5 ppm, respectively.[7] Comparison of the ^{13}C{^{1}H} NMR spectra of carbene complexes spanning a range of metals has shown a downfield shift for the carbenoid carbon that correlates well with the Lewis acidity of the metal, i.e., H > Be ≈ Al > Mg ≈ Ti.[26]

For **3** satellites due to ^{195}Pt coupling were discernible flanking each resonance in the ^{13}C{^{1}H} NMR spectrum (^{195}Pt, $I = {}^1/_2$, 33%). The largest coupling, by 2 orders of magnitude, is observed to the carbenoid carbon ($^1J_{^{195}\mathrm{Pt}-^{13}\mathrm{C}} = 1257$ Hz), which compares closely with that in the N-mesityl analogue of **3** (1218 Hz),[7] and is typical for ^1J to a σ-bonded carbon ligand.[27] The ^{195}Pt NMR spectrum of **3** comprises one resonance at −5390 ppm, which is discernible as a binomial quintet ($J = 10$ Hz) in the proton-coupled spectrum due to coupling to ligand backbone protons; the chemical shift in the ^{195}Pt NMR spectrum of bis(*N*,*N*′-dimesitylimidazol-2-ylidene)platinum is reported as −5729.1 ppm.[7] The value of the shift in these complexes is in agreement with, although not unequivocal proof of, the assigned oxidation state of zero: a value of between −4500 and −6000 ppm is

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Table 1. ^{1}H and ^{13}C{^{1}H} NMR Spectroscopic Data for L and Complexes 1, 2, and 3 (300 MHz, Benzene-d_6 Solutions)

	δ (ppm) ^{1}H NMR resonance			δ (ppm) ^{13}C{^{1}H} NMR resonance		
compound	NCC(ring)H	NC(CH_3)$_3$	C_{carbene}	NCC(ring)	NC(Me$_3$)	NC(CH$_3$)$_3$
L	6.76	1.52	212.6	115.0	55.7	31.4
[Ni(L)$_2$]	6.61	2.12	191.2	113.9	56.3	31.4
[Pd(L)$_2$]	6.74	2.11	194.4	113.9	57.3	32.0
[Pt(L)$_2$]	6.71	2.16	193.9	113.9	57.8	31.6

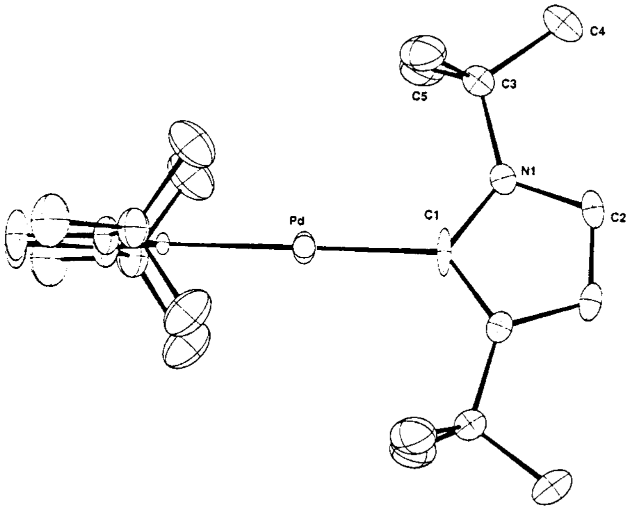

Figure 2. ORTEP[47] representation of the molecular structure of **2** (M = Pd). Thermal ellipsoids shown at 50% probability.

Table 2. Selected Distances and Angles for Complexes 2 and 3

	distance (Å)			angle (deg)	
bond	M = Pd	M = Pt	group	M = Pd	M = Pt
M−C(1)	2.041(6)	1.965(12)	C(1)−M−C(1′)	180.0	180.0
N(1)−C(1)	1.361(6)	1.384(11)	N(1)−C(1)−N(2)	105.3(6)	102.1(10)
N(1)−C(2)	1.374(9)	1.397(13)	C(1)−N(1)−C(2)	110.2(6)	111.4(9)
N(1)−C(4)	1.487(9)	1.49(2)	N(1)−C(2)−C(3)	107.1(4)	107.6(6)
C(2)−C(3)	1.36(2)	1.31(2)			

standard for a zerovalent complex, while resonances between −1000 and −5000 ppm are expected for Pt^{II} complexes, and anywhere between +7000 and −7000 ppm for Pt^{IV} complexes.[28,29]

Molecular Structure of Complexes 2 and 3. Crystals of **2** and **3** suitable for single-crystal X-ray structural determination were obtained by slowly cooling a toluene solution of each complex. An ORTEP view of the molecular structure of **2** (which is isostructural with **3**) is depicted in Figure 2, with selected bond lengths and angles collated in Table 2 for both complexes. In the solid state the metal center is linear and two-coordinate. The planes of the two ligand heterocycles are staggered by 90° in the structures, which permits steric protection of the metal center by the ligand *N*-*tert*-butyl groups. It is of interest that inspection of a space-filling model of **2** suggests the molecule is still remarkably sterically unencumbered.

The linear carbene−metal−carbene vector is crystallographically imposed upon each complex, and as such, the symmetry of the molecule approaches D_{2d}, with the torsion angle of 90° between the planes of the two ligands. This compares with a twist angle of 51° reported by Arduengo et al. for the N-mesityl-substituted analogue.[7] The C−M−C bond angle is also linear to within 3°, as in two other coordinate carbene complexes reported to date containing the metals Ag, Au, Ni, or Pt.[7,9] In the crystallographically characterized examples of homoleptic, linear, two-coordinate gold and silver carbene complexes, the twist angle appears to be governed predominantly by steric interactions and crystal-packing forces.[9,30,31]

Upon complexation, the imidazole ring skeleton retains planarity, but the N−C−N angle in **2** is relaxed from a value of 102.4° in the free ligand to 105.3°. Unusually, the value of the angle in **3** remains virtually unchanged within standard deviations. Other complexes of unsaturated N-heterocyclic carbenes that have been structurally characterized usually show an increase in this angle upon complexation by 2−5°. Thus the resultant angle in most complexes is usually intermediate between that in the free carbene and the corresponding imidazolium salt; these structural features are set out in Table 3. As has been observed in neutral complexes of an N-heterocyclic carbene, interatomic distances around the ring are longer in the complex than in the free carbene, but overall the backbone geometry of the ligand remains essentially unperturbed upon formation of either of the two complexes.

We have previously reported the results of gas-phase photoelectron spectroscopic studies on **2** and **3**, and it is salient that both the latter and the crystallographic results presented here strongly suggest that the bonding of the carbene ligand in **2** and **3** is predominantly σ in nature and that any π-bonding is minimal.[35]

Reaction of 2 with Dihydrogen. To obtain a measure of the steric saturation of the complexes, the reaction chemistry of these species with small molecules was briefly examined. A reaction between the di-*N*,*N*′-mesityl-substituted carbene analogues of **1** and **3** with dihydrogen had been alluded to previously, but not further reported on.[7] The reaction of the palladium compound reported here with dihydrogen was readily elucidated. Exposure of a yellow toluene solution of **2** to a dihydrogen atmosphere (1.5 bar) resulted in a change in color of the solution to grass green over a period of 2 h. This color faded, and a palladium mirror was observed to form on the walls of the reaction vessel

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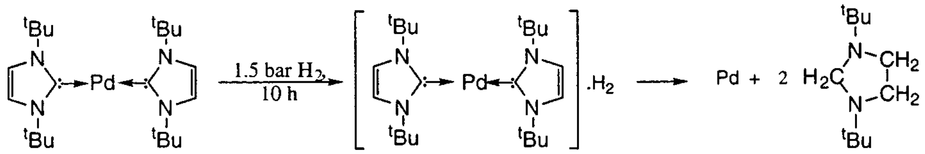
Table 3. Comparative Bond Lengths and Angles of L, the *N*-Mesityl Analogue, and N-Heterocyclic Carbene Complexes of Groups 9 and 10.

	bond lengths [Å] and angles [deg]				
compound	M−$C_{carbene}$[c]	N−$C_{carbene}$[d]	N−$C_{carbene}$−N	C−C(ring)	ref
L[e]		1.362	102.2(5)	1.341(2)	25
$[Pd(L)_2]$	2.041(6)	1.368	105.3(6)	1.36(2)	this work
$[Pt(L)_2]$	1.965(12)	1.391	102.1(10)	1.31(2)	this work
$[PdI_2(L_{Me})_2]$[b]	1.994	1.351			14
L_{mes}[a]		1.365	101.4(2)	1.331(5)	34
$[(L_{mes})H]^+$		1.336	109.2	1.339	34
$[Ni(L_{mes})_2]$	1.829	1.375	102.0	1.333	7
$[Pt(L_{mes})_2]$	1.951(8)	1.380(9)	102.5	1.316	7
$[Cu(L_{mes})_2]^+$	2.073	1.356	104.2	1.330	9
$[Ag(L_{mes})_2]^+$	2.014	1.328	104.1	1.327	9

[a] L_{Mes} = :C{N($C_6H_2Me_3$-2,4,6)CH}$_2$. [b] L_{Me} = :C{N(Me)CH}$_2$. [c] Mean. [d] Esd's included where given in original. [e] For structures of representative imidazolium salts see refs 7, 32, and 33

Scheme 1. Synthesis of Dihydroimidazole by Hydrogenation of the Pd-Coordinated Carbene



over the following 8 h until complete decolorization of the solution had occurred (Scheme 1). The solution remaining comprised only components of higher volatility than the free carbene ligand; an aliquot of the solution studied by GCMS showed the only significant components of this to be toluene and 1,3-bis-*tert*-butylimidazolidine, the product of hydrogenation of the ligand.

This procedure is effective in routinely achieving a 92% conversion of bound ligand to the dihydroimidazole 1,3-bis-*tert*-butylimidazolidine. Stirring a solution of L in toluene under the same volume and pressure of dihydrogen afforded no reaction after prolonged reaction times. Inspection of an aliquot taken from the reaction of **2** with dihydrogen after 2 h reaction time revealed three new resonances (of relative intensities 1:2:9 by integration) in the ^{1}H NMR spectrum, which remained of constant relative intensity until hydrogenation was completed, upon which they decreased to baseline. Presumably the green color derives from the intermediate metal-containing complex, although no resonance characteristic of a group 10 metal hydride was discernible above baseline in the ^{1}H NMR spectrum down to δ −50 ppm.

The complex **2** also shows reactivity toward ethene. Under a pressure (2.5 bar) of ethene, a benzene-d_6 solution showed reversible uptake of ethene, evidenced by shifted carbene resonances in the ^{1}H NMR spectrum, but the starting material was regenerated upon removal of the ethene pressure.

Some instructive comparisons may be drawn between these homoleptic carbene complexes with the related group 10 tertiary phosphine complexes. A wide range of homoleptic zerovalent complexes, particularly of Pd and Pt, have been characterized and studied as potential homogeneous catalysts for a wide range of organic transformations.[18,19,36] The members of the triad form zerovalent complexes of the type $[ML_4]$ (L = PPh_3, PEt_3), which undergo ligand dissociation in solution. The complex $[Pt(PPh_3)_2]$ can be isolated, but in the absence of additional donor molecules (with which it reacts readily to form complexes such as $[Pt(PPh_3)_2L]$, L = PPh_3, CO, PhCH=CHPh, PhC≡CPh) forms the complex $[\{Pt(PPh_3)_2\}_3]$, a symmetrical trimer with weak Pt−Pt bonds.[36] Only employment of the phosphines PCy_3 (Cy = cyclohexyl), PBu^t_3, $PPhBu^t_2$, or PPr^i_3 gives rise to the formation of a stable monomer $[Pt(PR_3)_2]$, and even then, from a concentrated solution of PCy_3, crystals of $[Pt(PCy_3)_3]$ have been isolated and show a greatly lengthened Pt−P bond (2.231(6) vs 2.303(6) Å for $[Pt(PCy_3)_2]$) and a tight intermeshing of the cyclohexyl groups (PCy_3 has a cone angle of 157°).[37,38]

The complexes **1**−**3** appear to be stable with respect to ligand dissociation processes in a solution in hydrocarbon solvents. Heating a sample of **1** to reflux in benzene-d_6 under the vapor pressure of the solvent resulted only in slight decomposition of the complex after 3 h; no evidence for the release of metal particles into the solution was found. Thus these zerovalent sterically unsaturated 14-electron complexes that are not susceptible to degradation by ligand dissociation processes may well prove useful as model species, or indeed as active catalysts.

Conclusion

The MVS technique has allowed the straightforward synthesis of homoleptic zerovalent carbene complexes in reasonable yields, one example of which, **2**, has been inaccessible to date by solution techniques. The 14-electron, coordinatively unsaturated complexes generated by the metal atom route can be synthesized, characterized, and reacted further with small molecules in the absence of any coordinating solvents or competing donor molecules at any point. The strong σ-donor characteristics of the N-heterocyclic carbene are clearly capable of stabilizing zerovalent complexes with little or no metal−ligand back-bonding, and the complexes

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Table 4. Co-condensation Synthesis Parameters for 1, 2, and 3

metal	evaporation power	mass evaporated	mass ligand introduced	color of matrix	yield of complex
nickel	320 W	0.19 g (3.2 mmol)	20 g (0.11 mol)	pale brown	10% (100 mg)
palladium	500 W	0.52 g (4.85 mmol)	26 g (0.14 mol)	pale yellow	32% (730 mg)
platinum	500 W	0.29 g (1.48 mmol)	16 g (0.09 mol)	pale yellow	25% (210 mg)

formed have been shown capable of further interesting reactions. Their reaction chemistry and potential catalytic utility, particularly that of the palladium complex **2**, are currently under investigation.

Experimental Details

All experimental procedures were carried out using standard high-vacuum and Schlenk techniques, under an atmosphere of dry argon, or under dinitrogen in an MBraun or a Miller-Howe glovebox.[39] Glassware and Celite 545 filter aid were flame-dried in vacuo prior to use. Solvents were dried and degassed by standard techniques prior to use.[40] Petroleum ether (bp 40−60 °C), referred to hereafter as hexanes, was distilled from sodium/potassium alloy and toluene from sodium metal under dinitrogen prior to use; benzene-d_6 was dried over potassium and then transferred to and stored in an ampule under dinitrogen prior to use. NMR spectra were recorded at 293 K on a 300 MHz spectrometer except for the ^{195}Pt spectrum, which was recorded on a 250 MHz spectrometer, with chemical shifts (δ) reported in ppm, relative to the residual proton chemical shifts of the internal deuterated solvent (^{1}H and ^{13}C) set relative to external TMS and external K_2PtCl_6 at 0 ppm (^{195}Pt). Coupling constants are quoted in hertz. Elemental analyses were performed by Canadian Microanalytical or A. T. Stones of the Department of Chemistry, University College of London.

Co-condensation experiments were carried out using the 50 l static reactor.[41] Modifications made to allow introduction of the ligand vapor into the machine were the replacement of Viton and Kalrez gaskets with Teflon in the inlet system and incorporation of an additional high-vacuum valve to facilitate loading of the ligand under an inert atmosphere.

Benzyltriethylammonium chloride, *tert*-butylamine, decolorizing charcoal, glycoaldehyde dimer, glyoxal solution, potassium *tert*-butoxide, and nickel, palladium and platinum metals were purchased from Aldrich Chemical Co. Potassium *tert*-butoxide was sublimed in vacuo, and *tert*-butylamine was distilled under dinitrogen prior to use. All metals were separately degassed prior to use, by melting under vacuum.

Ligand Synthesis. The synthesis and purification of 1,3-di-*tert*-butylimidazolium chloride precursor is described in the literature, although two modifications were made.[42] A portion of TEBA (benzyltriethylammonium chloride) (5 mol %) was added during the period of stirring before water elimination. After removal of water from the reaction mixture and before the temperature of the mixture fell below 50 °C the immiscible toluene layer was decanted from the viscous black tar in the flask; the tar was immediately dissolved in an equal volume of dry acetonitrile. After stirring this solution with decolorizing charcoal for 10 min and filtration to remove the charcoal, removal of volatiles under reduced pressure from the straw-colored filtrate yielded the imidazolium salt in 98% purity (by ^{1}H NMR spectroscopy). Total yields of 61% (300 g) were achieved routinely. The deprotonation step to synthesize 1,3-di-*tert*-butylimidazol-2-ylidene was according to literature methods.[25]

Bis(1,3-di-*tert*-butylimidazol-2-ylidene)M(0) (M = Ni (1), Pd (2), Pt (3)). In each experiment a metal pellet (0.19 g, 3.2 mmol) was evaporated using a positive hearth electron-beam gun (power input 320 W) and co-condensed with 1,3-di-*tert*-butylimidazol-2-ylidene over a period of 90 min. A colored matrix appeared in each case, whose color persisted on warming up to room temperature under a nitrogen atmosphere. A solution of the matrix was extracted from the vessel with hexanes (0.7 l) and filtered through a bed of Celite, and volatiles were removed from the filtrate under reduced pressure. After recovery of excess free ligand by sublimation (45 °C, 10^{-6} mbar) the resultant solid was extracted with pentane, filtered, and concentrated. Cooling of the respective solutions to −50 °C afforded brown crystals of bis(1,3-di-*tert*-butylimidazol-2-ylidene)nickel, **1**, yellow crystals of bis(1,3-di-*tert*-butylimidazol-2-ylidene)palladium, **2**, and dark yellow crystals of bis(1,3-di-*tert*-butylimidazol-2-ylidene)platinum, **3** (Table 4.).

Characterizing Data for 1. ^{1}H NMR (benzene-d_6): δ 6.61 (2H, s, NCC*H*), 2.12 (18H, s, NC(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 191.12 (s, N*C*N), 113.85 (s, N*C*C), 56.33 (s, N*C*(CH$_3$)$_3$), 31.44 (s, NC(*C*H$_3$)$_3$). MS (EI): *m*/*z* 418 (52, M$^+$), 180 (60, [^{t}Bu$_2$C:]$^+$). HRMS: *m*/*z* found 418.262694. Calculated for [$C_{22}H_{40}N_4Ni$]: 418.260645. Anal. Found: C, 61.71; H, 9.73; N, 12.77. Calculated for [$C_{22}H_{40}N_4Ni$]: C, 63.02; H, 9.62; N, 13.36. Characterizing Data for **2**. ^{1}H NMR (benzene-d_6): δ 6.74 (2H, s, NCC*H*), 2.11 (18H, s, NC(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 194.4 (s, N*C*N), 113.9 (s, N*C*C), 57.3 (s, N*C*(CH$_3$)$_3$), 32.0 (s, NC(*C*H$_3$)$_3$). MS (EI): *m*/*z* 466 (41, M$^+$), 286 (60, [M − ^{t}Bu$_2$C:]$^+$), 180 (74, [^{t}Bu$_2$C:]$^+$). Anal. Found: C, 56.67; H, 8.54; N, 12.22. Calculated for [$C_{22}H_{40}N_4Pd$]: C, 56.58; H, 8.63; N, 12.00. Characterizing Data for **3**. ^{1}H NMR (benzene-d_6): δ 6.71 (2H, s, NCC*H*), 2.16 (18H, s, NC(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 193.9 (s, $J_{^{195}\mathrm{PtC}} = 1257$ Hz, N*C*N), 113.9 (s, $J_{^{195}\mathrm{PtC}} = 56$ Hz, N*C*C), 57.8 (s, $J_{^{195}\mathrm{PtC}} = 25$ Hz, N*C*(CH$_3$)$_3$), 31.6 (s, $J_{^{195}\mathrm{PtC}} = 42$ Hz, NC(*C*H$_3$)$_3$). ^{195}Pt NMR (^{1}H decoupled) (benzene-d_6): δ −5390 (quin., $J_{^{195}\mathrm{PtH}} = 10$ Hz). MS (EI): *m*/*z* 555 (41, M$^+$), 498 (39, [M − ^{t}Bu]$^+$), 375 (36, [M − ^{t}Bu$_2$C:]$^+$), 180 (39, [^{t}Bu$_2$C:]$^+$). Anal. Found: C, 47.69; H, 7.30; N, 10.30. Calcd for [$C_{22}H_{40}N_4Pt$]: C, 47.55; H, 7.26; N, 10.08.

Reaction of 2 with Dihydrogen. A yellow solution of **2** (40 mg, 0.08 mmol) in toluene (100 mL) was stirred rapidly in a high-pressure ampule under an atmosphere of dihydrogen (1.5 bar). The solution changed in color from yellow to grass green over a period of 2 h and was completely decolorized after 10 h, leaving a palladium mirror on the walls of the ampule. All components in the solution were sufficiently volatile to be removed at 30 °C, 10^{-2} mbar. Isolation of the colorless volatiles yielded a toluene solution of an organic compound characterized as the uncomplexed, fully hydrogenated derivative of L, 1,3-bis-*tert*-butylimidazolidine, by GC−MS and ^{1}H NMR spectroscopy. A total yield of 92% was obtained. A colorless solution of L (18.0 mg, 0.10 mmol) in toluene (50 mL) was stirred in a high-pressure ampule under an atmosphere of dihydrogen (1.5 bar) as above. After a period of 10 h both ^{1}H NMR spectroscopy and EI MS analysis of the reaction components confirmed that no reaction had occurred. Characterizing Data for 1,3-bis-*tert*-butylimidazolidine. ^{1}H NMR (benzene-d_6): δ 3.68 (2H, s, NC*H*$_2$N), 2.74 (4H, s, NC*H*$_2$CH$_2$), 1.03 (18H, s, NC(C*H*$_3$)$_3$). ^{13}C-

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$\{^1H\}$ NMR: δ 63.2 (s, N*C*N), 52.0 (s, N*C*(CH$_3$)$_3$), 45.9 (s, N*C*C), 26.0 (s, NC(*C*H$_3$)$_3$). GC−MS (EI): *m*/*z* 184 (20, M$^+$), 169 (25, [M − Me]$^+$), 127 (25, [M − ^{t}Bu]$^+$), 113 (85, [M − N(^{t}Bu)$_3$]$^+$), 71 (72, [N(^{t}Bu)$_3$]$^+$).

Reaction of 2 with Ethene. A yellow benzene-d_6 solution of **2** (25 mg, 0.05 mmol, 0.5 mL) was degassed and charged with an atmosphere of high-purity ethene (2.5 bar). The intensity of the yellow color of the original solution decreased over a period of hours, and the formation of an ethene adduct was observed by ^{1}H NMR spectroscopy to proceed with a half-life of 18 h at 298 K. Removal of the gas pressure resulted in complete reversion to the starting material. Characterizing data for [**2**·(CH$_2$=CH$_2$)$_n$]. ^{1}H NMR (d_6-benzene): δ 6.79 (1H, s, NC*H*C), 1.40 (9H, s, NC(C*H*$_3$)$_3$). $^{13}C\{^1H\}$ NMR: 120.2 (s, N*C*C), 35.5 (s, NC(*C*H$_3$)$_3$).

X-ray Structure Determination of 2. Crystals of **2** of sufficient quality for single-crystal X-ray determination of the molecular structure were grown from a saturated toluene solution at −20 °C. Data were collected on an Enraf-Nonius CAD4 diffractometer using a crystal of dimensions 0.3 × 0.3 × 0.3 mm mounted in a 0.5 mm Lindemann capillary at 293(2) K. A total of 1006 unique reflections were measured for $2° < 2\theta < 25°$, 540 reflections with $|F^2| > 2\sigma(F^2)$ being used in the refinement, where $\sigma(F^2) = [\sigma^2(I) + (0.04i)^2]^{0.5}/L_p$. The structure was solved and refined as isomorphous with **3** (vide infra). All non-H atoms were anisotropic. Hydrogen atoms were refined in riding mode with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$ for methyl groups. Interactive graphics and final drawing were obtained using CAMERON.[43−46] Crystal data are given in Table 5.

X-ray Structure Determination of 3. Crystals of **3** of sufficient quality for single-crystal X-ray determination of the molecular structure were grown from a saturated toluene solution cooled to −20 °C. Data were collected on an Enraf-Nonius CAD4 diffractometer using a crystal of dimensions 0.3 × 0.3 × 0.1 mm mounted in a 0.5 mm Lindemann capillary at 293(2) K. A total of 609 unique reflections were measured for $2° < 2\theta < 25°$, 330 reflections with $|F^2| > 2\sigma(F^2)$ being used in the refinement, where $\sigma(F^2) = [\sigma^2(I) + (0.04i)^2]^{0.5}/L_p$. The structure was solved using SHELXS-86 and refined using SHELXL-93 with non-H atoms refined anisotropically by full-matrix least-squares. Hydrogen atoms were refined in riding mode with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$ for methyl groups. Interactive graphics and final drawing were obtained using CAMERON.[43−46] Crystal data are given in Table 5.

Table 5. Crystallographic Details

	2	3
empirical formula	$C_{22}H_{40}N_4Pd$	$C_{22}H_{40}N_4Pt$
cryst syst, shape	tetragonal, _yellow block	tetragonal, _yellow block
space group	142*m* (No. 121)	142*m* (No. 121)
temp (K)	293(2)	293(2)
a (Å)	10.080(6)	9.950(4)
b (Å)	10.080(6)	9.950(4)
c (Å)	11.907(13)	11.786(5)
α (deg)	90	90
β (deg)	90	90
γ (deg)	90	90
V (Å^3)	1210(2)	1166.8(8)
Z	2	4
density$_{calc}$ (Mg/m^3)	1.28	1.58
radiation (λ (Å))	Mo Kα (0.71073)	Mo Kα (0.71073)
fw (g/mol)	467.0	555.0
μ (mm^{-1})	0.78	6.03
range 2−2θ (deg)	25	25
F(000)	492	556
R1 (all data)	0.056	0.028
wR2 (all data)	0.117	0.059
S	1.018	1.036

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Supporting Information Available: Tables of crystal and intensity data, complete fractional atomic coordinates, interatomic distances and angles, anisotropic thermal displacement parameters, and fully labeled ORTEP figures for **2** and **3**; NMR spectra of **2** with H$_2$ and C$_2$H$_4$ (16 pages).

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