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PAPER

Correlation of spectroscopically determined ligand donor strength and nucleophilicity of substituted pyrazoles†

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The relative ligand donor strengths of 10 pyrazole-derived ligands has been determined with great accuracy, making use of the interdependence between the donor strength of the co-ligand and the ^{13}C NMR chemical shift of the $^{i}Pr_2$-bimy carbene signal in *trans*-[$PdBr_2$($^{i}Pr_2$-bimy)L] complexes ($^{i}Pr_2$-bimy = 1,3-diisopropylbenzimidazolin-2-ylidene; L = pyrazole-derived ligand). Even subtle variations in the substitution pattern of the pyrazole backbone up to three bonds away from the coordinating nitrogen could be detected reliably using this methodology. Alkylation experiments conducted on the pyrazoles using electrophiles of varied reactivity (ethyl bromide, ethyl iodide, and trimethyloxonium tetrafluoroborate) served as a benchmark to rank the pyrazoles in three groups of gradually increasing nucleophilicity, which correlated well with their determined donor strength.

Introduction

The catalytic properties of transition metal complexes can be fine-tuned by carefully choosing ligands of appropriate steric demand and donor strength. In order to facilitate rational catalyst design, on-going efforts have been made to provide a reliable scale to compare the donor abilities of Werner-type and organometallic ligands. This development is still in progress, and up to now, several methodologies have emerged.[1]

The most commonly used experimental procedure, introduced by Tolman, relies on the determination of the CO A_1 band in IR spectra of [$Ni(CO)_3$L] complexes, which in turn is directly influenced by the amount of Ni–CO backdonation induced by the electron donation of the ligand L.[2] While Tolman's electronic parameter (TEP) is indicative of the donating ability of a wide range of phosphines, which are among the most widely used ligands in transition metal catalysis, most Werner-type and other ligands of interest cannot be easily characterized that way. Furthermore, the synthesis of [$Ni(CO)_3$L] complexes requires the handling of highly toxic [$Ni(CO)_4$], making the determination of donor strength by this route potentially hazardous. To address this concern, the TEP concept has been recently extended and correlated to the Rh(I) and Ir(I) complexes [$MX(CO)_2$L] (M = Rh, Ir; X = halide).[3] Nevertheless, ligands of interest that compete with the COs for π-backdonation generally pose a problem in all CO-based methodologies.

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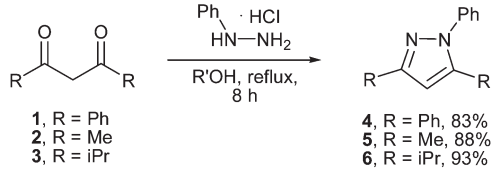
†Electronic supplementary information (ESI) available: ^{1}H and ^{13}C NMR spectra, experimental procedures, CIF files for complexes **17**, **20**, **21** and **25**. CCDC 870361–870364. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt30526g

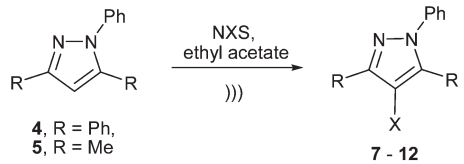
An alternative electronic parameter, introduced by Lever, correlates the E_0 value of a redox couple (most commonly Ru^{II}/Ru^{III}) of complexes which incorporate the ligands of interest with the donor abilities of these ligands.[4] Lever's electronic parameter (LEP) is available for a wide range of Werner-type ligands. Comparison between these two scales is difficult, since only for a handful of ligands both the TEP and the LEP values have been determined.[5]

More recently, we have proposed a versatile new electronic parameter based on the chemical shift of the carbene carbon in complexes of the type *trans*-[$PdBr_2$($^{i}Pr_2$-bimy)L], which allows easy determination of both Werner-type and organometallic ligands.[6] A higher donor strength of the transoid ligand L leads to a reduction in the Lewis acidity of the metal centre, which in turn leads to a downfield shift of the carbene carbon in the $^{i}Pr_2$-bimy ligand. Such an effect has been observed before,[7] and allows a direct assessment of the donor strength by a simple ^{13}C NMR spectroscopic measurement. In contrast to IR spectroscopy or electrochemical measurements, ^{13}C NMR spectra exhibit very sharp resonances, allowing for a highly improved accuracy in the determination of the electronic parameter as compared to TEP and LEP. Moreover, the required complex probes can be easily prepared by reacting the ligand of interest with the readily available dimeric complex [$PdBr_2$($^{i}Pr_2$-bimy)]$_2$ in high yields without any toxic and hazardous chemicals involved.[8] The determination of the electronic parameter can be achieved *via* a simple, non-destructive and routine measurement.

In order to exploit this improved accuracy of measurement and in search for suitable ligand precursors for mesoionic pyrazolin-4-ylidenes,[9] we decided to explore the donor strength of a series of substituted pyrazoles bearing a variety of halogen, alkyl, and aryl substituents as well as exocyclic O- and N-donor atoms.



Scheme 1 Synthesis of pyrazoles.



Scheme 2 Halogenation under ultrasound irradiation (X = Cl, Br, I).

In a further step, we assessed the nucleophilicity of the N-donor by reacting the free ligand with various electrophiles. Most nucleophilicity parameters rely either on DFT calculations or more often on kinetic measurements.[10] These scales allow for a quantitative and precise comparison of a multitude of nucleophiles, but the determination of values calls for precise measurements of kinetic data or extensive calculations. Our simple experiment might close the gap in the methodology, if only a quick and qualitative determination of nucleophilicity is needed.

Results and discussion

Pyrazoles

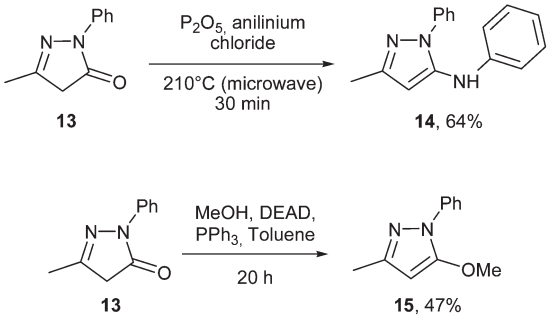
Since the discovery of the Knorr pyrazole synthesis, several procedures for the synthesis of pyrazoles have emerged due to the widespread application of substituted pyrazoles in medicinal chemistry and as ligands in coordination chemistry.[11,12] Drawing from these procedures, the desired pyrazoles were made. Starting from commercially available 1,3-diketones, a condensation reaction with phenylhydrazine hydrochloride gave the desired alkyl and aryl pyrazoles in good yields (Scheme 1). Pure products were obtained either by recrystallization (**4**) or by distillation of the crude mixture (**5** and **6**).

The introduction of a halogen substituent in the 4-position on the pyrazole scaffold is possible by treating the compound with bromine or iodine directly.[13] However, prolonged reaction times of several days and harsh reaction conditions were needed in order to reach full conversion of the starting materials. We therefore turned to a mild and efficient procedure described by Pereira *et al.* who described the halogenation of pyrazoles by *N*-halosuccinimides under ultrasound irradiation.[14] These conditions generally yielded the desired halogenated pyrazoles in excellent yields (Scheme 2). In the case of 1-phenyl-3,5-dimethyl-1*H*-pyrazole (**5**) however, the reaction with *N*-chlorosuccinimide gave a complex mixture of side-chain halogenated compounds, which is in contrast with the findings of Pereira and co-workers. On the other hand, the bromination and iodination reaction of **5** proceeded without any such complication and gave the desired products exclusively (Table 1).[15]

Table 1 Halogenation of the pyrazole scaffold

Entry	Substrate	R	X	Product	Yield
1	**5**	Me	Cl	**7**	—[a]
2	**5**	Me	Br	**8**	96%
3	**5**	Me	I	**9**	95%
4	**4**	Ph	Cl	**10**	>99%
5	**4**	Ph	Br	**11**	>99%
6	**4**	Ph	I	**12**	92%

[a] Only side-chain halogenation observed.



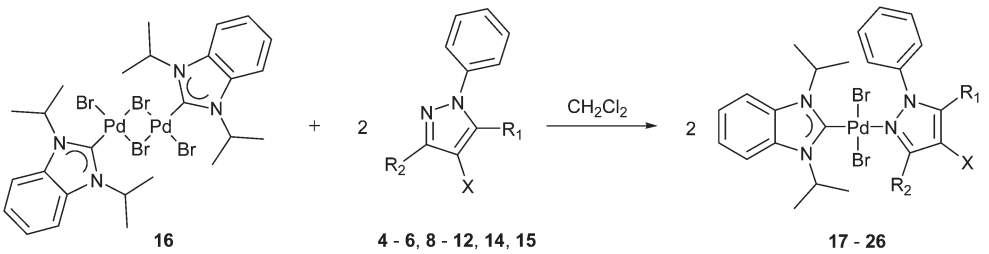
Scheme 3 Synthesis of donor-functionalized pyrazoles.

In order to introduce greater diversity into the series of tested pyrazoles, we included donor-substituted pyrazoles. Unfortunately, the synthesis of this class of compounds is less straightforward than the procedure for their alkyl- or aryl-substituted counterparts. While the reaction of 1,3-diketones with phenylhydrazine hydrochloride readily yields the corresponding pyrazoles, a similar reaction with β-ketoesters or β-ketoamides leads to the formation of pyrazolin-5-ones, along with a small amount of the desired pyrazoles with donor-functionalities in the 5-position.[16] A synthetically simple method for the formation of 5-aminopyrazoles published by Dodd and Martinez, who performed the cyclisation reaction in the presence of Lawesson's reagent, thus generating a β-ketothioamide *in situ*, failed to give the desired products in our syntheses.[17] An attempt to extend their methodology to the conversion of β-ketoesters proved equally futile. We therefore sought to use the commercially available 1-phenyl-3-methyl-pyrazolin-5-one **13** as a starting material.

The direct conversion of **13** to **14** can be effected by heating it in the presence of a dehydration agent and anilinium chloride.[18] Making use of the known advantages of microwave accelerated chemistry, we could further improve this procedure, and were able to obtain **14** in satisfactory yield. Finally, the methoxy functionalized pyrazole **15** was obtained from **13** by Mitsunobu condensation (Scheme 3).[19,20]

Palladium complexes and donor strength determination

The ^{13}C chemical shift of the carbene carbon in complexes of the type *trans*-dibromo(1,3-diisopropylbenzimidazolin-2-ylidene)-(pyrazole)palladium(II) **17–26** was used as a measure of donor strength. In these complexes, a higher donor ability of the



16 4 - 6, 8 - 12, 14, 15 17 - 26

Scheme 4 Cleavage of the dimeric palladium precursor complex.

transoid pyrazole ligand is bound to decrease the Lewis acidity of the metal centre, which in turn leads to a downfield shift of the NMR resonance for the carbene carbon.[6,7] The desired complexes can be prepared in analogy to similar complexes prepared previously in our group by cleavage of the dimeric species **16** (Scheme 4).[8,21]

Complexes **17–26** could be obtained from **16** in high to quantitative yields without the necessity of any purification step. All compounds are light yellow solids that are readily soluble in chlorinated organic solvents, but insoluble in diethyl ether and alkanes.

Upon cleavage of **16**, the isopropyl moieties in the NHC ligand are no longer spectroscopically equal, and thus two sets of isopropyl signals are present in the ^{1}H NMR spectra. Compared to the starting material, where the isopropyl methine proton resonates at 6.54 ppm, a pronounced upfield shift of up to 1.4 ppm is observed. It is noteworthy that in complexes **17–26**, the methine proton resonance varies between 5.07 and 6.26 ppm, with one of the two resonances being pronouncedly more upfield shifted than the other. The phenyl substituent on the pyrazole ligand exerts a shielding influence on one methine proton, leading to the observed change in chemical shift. A similar aryl substituent-induced upfield shift in complexes with a hindered rotation along the metal–ligand axes has been observed by us previously.[22] The resonance for the methyl groups of the isopropyl moiety is less affected, with a comparatively small upfield shift of ~0.4 ppm and a smaller gap between the two resonances. The ring protons in the pyrazole ring were shifted downfield by ~0.1 ppm in the case of the simple pyrazoles **4–6**, while the donor-substituted pyrazoles showed an upfield shift of ~0.3 ppm. While the former can be attributed to the deshielding effect of complexation, the latter could be caused by a stronger mesomeric effect in the coordinated pyrazoles.

The observed ^{13}C NMR chemical shifts of the carbene carbon in these complexes differ in a narrow range of 2.3 ppm, with complex **23** exhibiting the lowest value of δ = 160.8 ppm and complex **19** the highest value of δ = 163.1 ppm (Table 2, entries 3 and 7). Nevertheless, all complexes can be distinguished unambiguously by their characteristic NMR shifts (Fig. 1). The obtained values are in good agreement with previously observed chemical shifts for similar complexes. For example, an imidazole analogue of complexes **17–26** exhibits a chemical shift of the carbene carbon of δ = 161.4 ppm, while a complex bearing a more weakly donating pyridine ligand was found to give rise to a resonance signal at δ = 160.0 ppm.[6]

The observed chemical shifts, and thus the experimentally determined donor strengths of the substituted pyrazoles are in good agreement with predictions based on the inductive effects of the various substituents. In the case of pyrazoles without a halogen substituent in the 4-position, the diisopropyl substituted pyrazole shows the best donor abilities, followed by the dimethyl substituted system, and the diphenyl substituted system exhibiting the lowest donor strength (entries 1–3). This is in line with a decreasing + *I* effect of the substituents in the order ^{i}Pr > Me > Ph. The N- and O-substituted pyrazoles have an intermediate donor strength in this series, reflecting the competing influences of −*I* and +*M* effect exerted by these substituents.

The introduction of halogen substituents generally leads to an upfield shift of the carbene carbon resonance in the case of both dimethyl and diphenyl substituted pyrazoles. The observed upfield shift is greater for a more electronegative bromo- compared to an iodo-substituent. A notable exception is entry 6. The chloro-substituted pyrazole complex has a carbene carbon resonance at δ = 160.9 ppm, while the bromo-derivative has the lower value of δ = 160.8 ppm (entries 6 and 7) implying that the chloropyrazole may be a slightly stronger donor. At first sight, it seems that our system is not able to reflect the electronic properties of these two halopyrazoles with absolute certainty. However,

Table 2 Synthesis of pyrazole complexes and $^{13}C_{carbene}$ NMR shifts

Entry	R^1	R^2	X	Product	Yield	δ $C_{carbene}$ (ppm)
1	Me	Me	H	**17**	87%	163.0
2	Ph	Ph	H	**18**	95%	161.6
3	^{i}Pr	^{i}Pr	H	**19**	>99%	163.1
4	Me	Me	Br	**20**	98%	161.8
5	Me	Me	I	**21**	>99%	161.8
6	Ph	Ph	Cl	**22**	>99%	160.9
7	Ph	Ph	Br	**23**	>99%	160.8
8	Ph	Ph	I	**24**	98%	160.9
9	OMe	Me	H	**25**	>99%	162.6
10	NHPh	Me	H	**26**	>99%	162.8

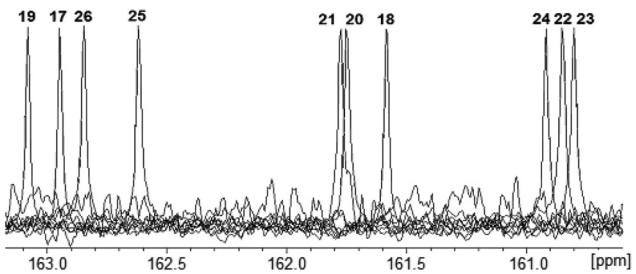


Fig. 1 ^{13}C NMR resonances of $C_{carbene}$ in **17–26**.

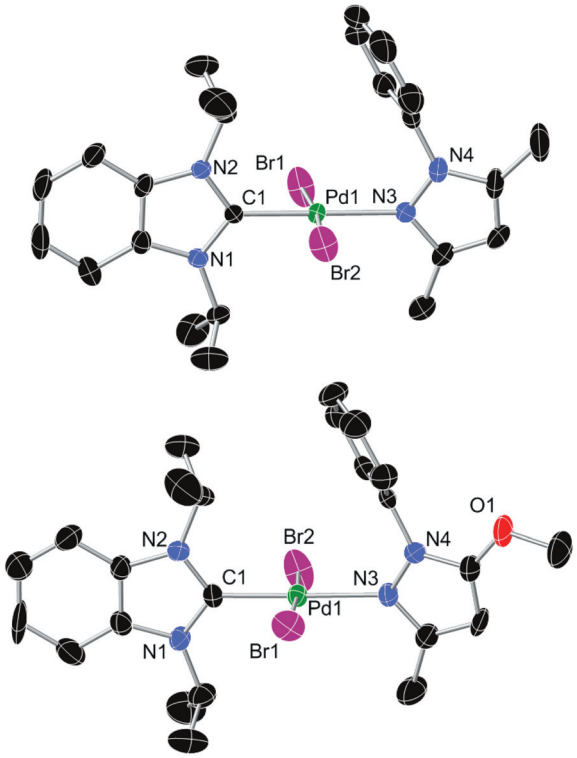


Fig. 2 Molecular structures of **17** and **25** (hydrogen atoms have been omitted for clarity, thermal ellipsoids at 50% probability).

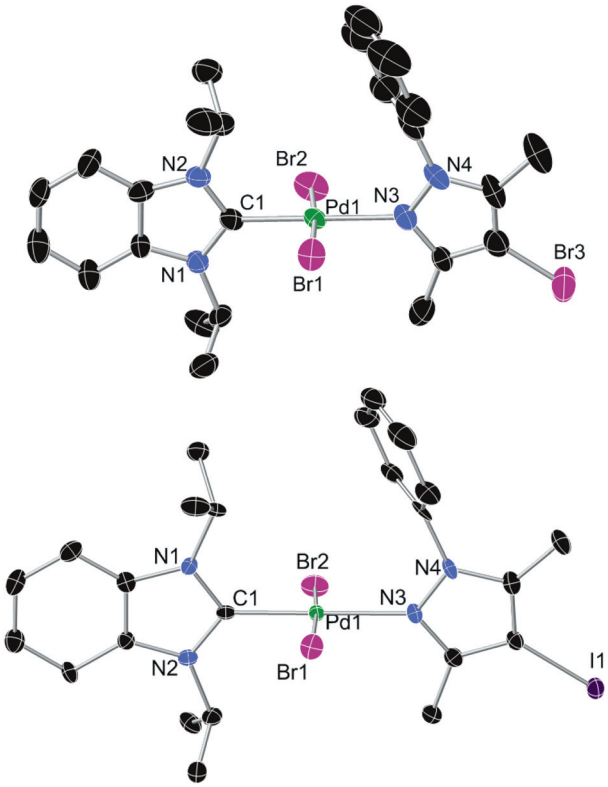


Fig. 3 Molecular structures of **20** and **21** (hydrogen atoms and solvent molecules have been omitted for clarity, thermal ellipsoids at 50% probability).

the different contributions of $-I$ *versus* $+M$ effects in Br *versus* Cl may offer an explanation for this observation. Although the Cl atom has a greater $-I$ effect compared to Br, its smaller size may offer better orbital overlap with carbon enhancing its $+M$ effect, which in turn can compensate its $-I$ effect. For the bigger Br and I atoms, a smaller contribution of the $+M$ effect is expected. Taking this into consideration, there is good agreement with the theoretical predictions of donor strength and the experimentally determined values.

Crystal structures

Single crystals suitable for X-ray diffraction studies were obtained for an exemplary selection of complexes by slow diffusion of diethyl ether in a saturated chloroform solution. Fig. 2 and 3 depict the molecular structures of complexes **17** and **25**, and **20** and **21**, respectively. Crystallographic data is given in Table 3 and selected bond parameters are listed in table, and a selection of crystallographic data is given in Table 4.

In each case, palladium has a slightly distorted square-planar coordination geometry, in which the NHC and the pyrazole are *trans* to each other. This is in line with the observations made on previously synthesized systems, and reflects the tendency to avoid a sterically more crowded *cis*-configuration. The planes of the benzimidazolin-2-ylidene and the pyrazole ligand are almost parallel, with small dihedral angles ranging from 5–14°. The phenyl substituent on N(4) is twisted out of the pyrazole plane by 50–64° in order to avoid unfavourable steric interaction with the isopropyl groups on the NHC ligand.

The Pd–$C_{carbene}$ bond distances fall into the narrow range of 1.943(5) Å to 1.953(6) Å, while Pd–N bonds show marginally more variation and range from 2.090(4) Å to 2.108(5) Å. These values are in good agreement with bond lengths in similar systems. For instance, with a pyridine ligand in the *trans*-position, the Pd–$C_{carbene}$ bond was found to be 1.953(4) Å long, and the Pd–N bond 2.113(3) Å, while imidazole and methylimidazole gave Pd–$C_{carbene}$ bond lengths of 1.943(2) Å and 1.952(3) Å, as well as 2.097(2) Å and 2.105(3) Å for the Pd–N bonds.[6,7c]

Alkylation experiments

To determine the approximate nucleophilicity of the substituted pyrazoles, the reactivity with three electrophiles of increasing strength was tested (Scheme 5). Trimethyloxonium tetrafluoroborate is an extremely strong alkylation agent, and it was expected that it would alkylate all pyrazoles irrespective of the electron density at N2. Ethyl iodide, while still being a strong alkylation agent, is nevertheless somewhat less electrophilic than Meerwein's salt, and ethyl bromide is even less reactive. Based on previously developed procedures, the pyrazoles were subjected to test reactions by heating them in an excess of neat ethyl halide, or by exposing them to trimethyloxonium tetrafluoroborate in anhydrous dichloromethane.

As anticipated, all pyrazoles under scrutiny with the exception of **14** were smoothly alkylated by trimethyloxonium tetrafluoroborate, albeit no correlation between the yields of pyrazolium salts and the determined donor strength of their parent pyrazoles

Table 3 Selected crystallographic data, data collection and refinement parameters

	17	**25**	**20**·$CHCl_3$	**21**·$CHCl_3$
Formula	$C_{24}H_{30}Br_2N_4Pd$	$C_{24}H_{30}Br_2ON_4Pd$	$C_{25}H_{30}Br_3Cl_3N_4Pd$	$C_{25}H_{30}Br_2Cl_3IN_4Pd$
M_w (g mol^{-1})	640.76	656.75	839.01	886.00
Colour, habit	Yellow plates	Yellow needles	Yellow needles	Yellow needles
Crystal size (mm)	0.50 × 0.30 × 0.06	0.60 × 0.20 × 0.08	0.50 × 0.26 × 0.10	0.26 × 0.22 × 0.16
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Pbca*	*Pbca*	$P2_12_12_1$	$P2_12_12_1$
a (Å)	9.0480(3)	9.0465(6)	11.706(4)	11.741(2)
b (Å)	16.4781(6)	16.5328(10)	15.947(5)	15.964(3)
c (Å)	35.4180(14)	35.937(2)	16.887(6)	16.643(3)
α (°)	90	90	90	90
β (°)	90	90	90	90
γ (°)	90	90	90	90
V (Å^3)	5280.6(3)	5374.9(6)	3152.3(18)	3119.5(10)
Z	8	8	4	4
$\rho_{calculated}$ (g cm^{-3})	1.612	1.623	1.768	1.886
Temperature (K)	223(2)	223(2)	223(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
θ (°)	1.15 to 27.49	2.27 to 27.50	1.76 to 27.50	1.77 to 27.50
No. of unique reflections	6056	6171	7213	7164
Max. and min. transmission	0.8064, 0.2559	0.7569, 0.2158	0.6526, 0.2037	0.5379, 0.3925
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0647$, w$R_2 = 0.1242$	$R_1 = 0.0697$, w$R_2 = 0.1552$	$R_1 = 0.0538$, w$R_2 = 0.1173$	$R_1 = 0.0360$, w$R_2 = 0.0930$
R indices (all data)	$R_1 = 0.0845$, w$R_2 = 0.1314$	$R_1 = 0.0987$, w$R_2 = 0.1648$	$R_1 = 0.0953$, w$R_2 = 0.1337$	$R_1 = 0.0392$, w$R_2 = 0.0945$
Goodness-of-fit on F^2	1.199	1.141	0.943	1.068
Peak/hole (e Å^{-3})	1.107 and −1.129	2.679 and −1.165	1.544 and −0.686	1.342 and −1.000

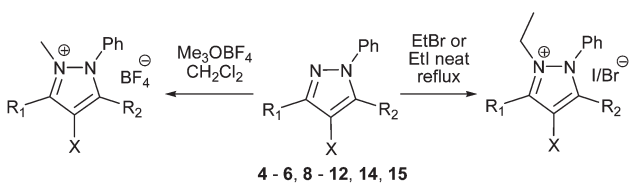
Table 4 Selected interatomic distances (Å) and angles (°)

	17	**25**	**20**·$CHCl_3$	**21**·$CHCl_3$
Pd(1)–C(1)	1.943(5)	1.953(6)	1.950(8)	1.947(5)
Pd(1)–Br(1)	2.4277(7)	2.4346(10)	2.4159(12)	2.4066(8)
Pd(1)–Br(2)	2.4266(7)	2.4251(10)	2.4164(12)	2.4063(8)
Pd(1)–N(3)	2.090(4)	2.108(5)	2.107(6)	2.097(4)
C(1)–Pd(1)–Br(1)	87.97(14)	87.79(19)	88.4(2)	88.21(15)
C(1)–Pd(1)–Br(2)	87.33(14)	87.76(19)	87.6(2)	88.52(16)
Br(1)–Pd(1)–N(3)	92.95(13)	91.36(17)	90.97(17)	91.35(12)
Br(2)–Pd(1)–N(3)	91.76(13)	93.13(17)	93.09(17)	91.94(13)
C(1)–Pd(1)–N(3)	178.93(19)	178.5(3)	179.3(3)	179.5(2)
Br(1)–Pd(1)–Br(2)	174.75(3)	174.94(4)	175.40(4)	175.25(3)
N(2)–C(1)–N(3)–N(4)	13.89	14.08	10.09	5.33
N(3)–N(4)–C(19)–C(20)	64.42	49.89	58.55	58.05

could be observed. The unsystematic variation in yields can be attributed to losses during the often difficult work-up of the crude alkylation product, which was usually obtained along with oily byproducts of unknown nature. Washing steps were required to obtain analytically pure products, and slightly different properties of the different pyrazolium salts can explain the unpredictable losses in yield during this process. In the extreme case of pyrazole **14** with an aminophenyl substituent in 5-position, only a black oil could be obtained, from which no pyrazolium salt could be isolated.

No clear trend in yield was observed as well for the alkylation with ethyl iodide, albeit more electron-rich pyrazoles gave somewhat higher yields than electron-poor systems. Notably, the four most electron-deficient pyrazoles **4** and **10–12** were not alkylated despite the harsh conditions, long reaction times, and large excess of alkylating agent (Table 5, entries 1–4). Apparently, these four pyrazoles can only be alkylated by the strongest electrophile, which in turn underscores their low nucleophilicity.

In the case of the 5-methoxypyrazole **15** (entry 7), no alkylation was observed. Instead, only small amounts of a transesterification product could be isolated, in which the methoxy group had been replaced by an ethoxy group.



Scheme 5 Alkylation of pyrazoles.

The weakest electrophile, ethyl bromide, showed no reaction with most pyrazoles. Only the two most electron-rich pyrazoles gave small to trace amounts of alkylation product, but even after heating to reflux for 3 days, only partial conversion was observed. In the case of **6**, which gave a lower yield than **4**, the steric influence exerted by the bulky isopropyl substituent in the α-position to the nucleophilic nitrogen certainly had an adverse effect on the reactivity.

Based on these alkylation experiments, the pyrazoles can be divided into three groups. Fig. 4 shows that there is a good correlation between their nucleophilicity and their donor strength as determined by ^{13}C NMR spectroscopy. From this consistent agreement, it is reasonable to assume that there exists an interdependence between the donor strength – and thus, the electron density at N2 – and the transition state energy for alkylation reactions.

Pyrazoles that give rise to a carbene carbon resonance in *trans*-[$PdBr_2$(^{i}Pr_2-bimy)(pyrazole)] upfield from 161.6 ppm are the weakest donors in the series under investigation and can only be alkylated using Meerwein's salt. If the carbene carbon chemical shift falls in the range of 161.6–162.9 ppm, which corresponds to an intermediate donor strength, both ethyl iodide and trimethyloxonium tetrafluoroborate react readily with the pyrazole, and if the chemical shift is even higher, even ethyl bromide can alkylate the pyrazoles.

Table 5 Alkylation experiments

Entry	Nucleophile	Electrophile		
		EtBr	EtI	Me_3OBF_4
1	**11**	0%	0%	70%
2	**10**	0%	0%	37%
3	**12**	0%	0%	67%
4	**5**	0%	0%	55%
5	**8**	0%	24%[b]	51%
6	**9**	0%	50%[a]	80%
7	**15**	0%	Decomposition[c]	62%
8	**14**	0%	58%	Decomposition[d]
9	**4**	7%[b]	99%	77%
10	**6**	Trace[b]	75%	71%

[a] From ref. 28. [b] Obtained as a mixture of product and starting material; yield determined by ^1H NMR spectroscopy. [c] Methoxy group was cleaved under reaction conditions, no alkylation product obtained. [d] Black polymeric material was obtained.

Conclusion

In conclusion, we have been able to demonstrate that even subtle variations of donor strength in pyrazole ligands can be detected with great accuracy by our previously developed electronic parameter based on the ^{13}C NMR chemical shift of the carbene carbon in *trans*-[$PdBr_2$(^{i}Pr_2-bimy)L] complexes. A good correlation between these experimentally determined donor strength values and the nucleophilicity of the nitrogen donor atom in the pyrazoles has been observed in alkylation experiments. This indicates that our methodology is useful not only for donor strength determinations, but also for semi-quantitative predictions of the reactivity of nucleophiles. While kinetic measurements give accurate information about the nucleophilicity of a reactive centre, these measurements are not easily performed. In contrast, our method is fast, safe and non-destructive, and the obtained information is of sufficient accuracy in many cases.

Further investigations should focus on nucleophiles other than pyrazoles, as well as on other electrophiles. Of special interest is the extension of the reactivity scale towards more reactive nucleophiles, and thus, less reactive alkylating agents.

Experimental section

General considerations

All reactions were carried out without precautions to exclude air and moisture, unless stated otherwise. Solvents were used as received or dried using standard procedures. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV 300 spectrometer. The chemical shifts are given relative to tetramethylsilane with the solvent serving as internal standard for calibration ($CHCl_3$, δ = 7.26 ppm [^1H] and δ = 77.70 ppm [^{13}C]). Mass spectra were measured using a Finnigan LCQ spectrometer (ESI). Elemental analyses were performed by the Chemical, Materials and Molecular Analysis Centre at the Department of Chemistry, National

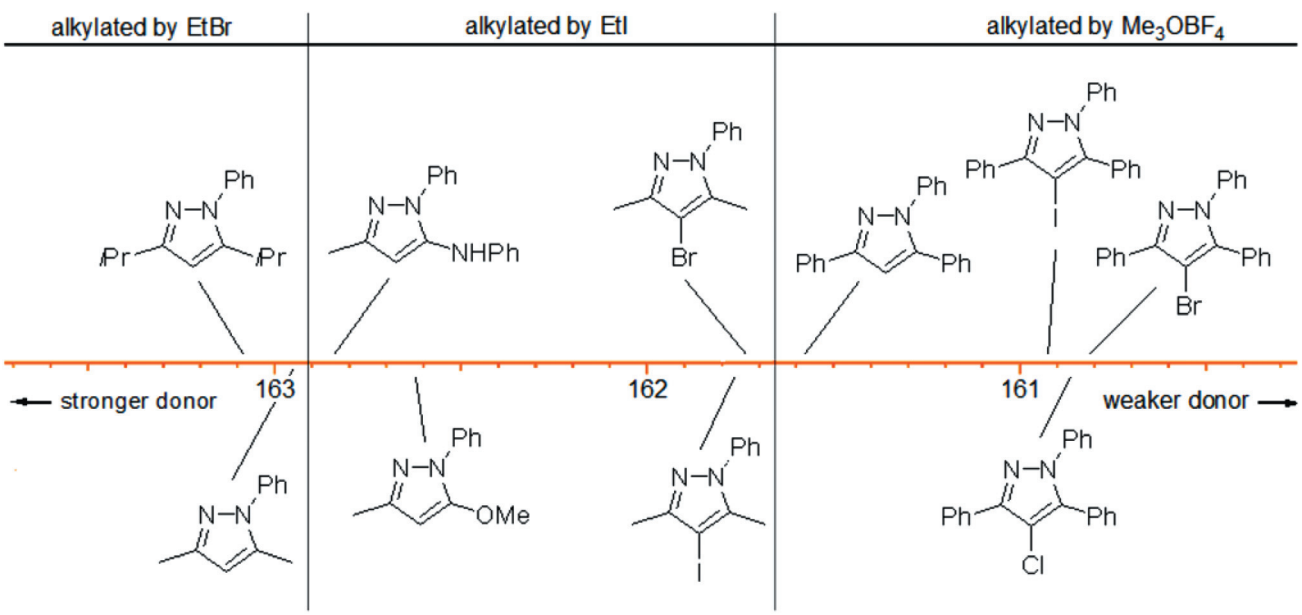


Fig. 4 Correlation between the electronic parameter and the reactivity towards electrophiles.

University of Singapore. Di-μ-bromo-bis(1,3-diisopropylbenzimidazolin-2-ylidene)-dibromo-dipalladium(II) (**16**) was prepared according to a literature procedure.[8]

Syntheses

4-Chloro-1,3,5-triphenyl-1*H*-pyrazole (10). 1,3,5-Triphenyl-1*H*-pyrazole (**4**) (500 mg, 1.68 mmol, 1.00 eq) and *N*-chlorosuccinimide (561 mg, 4.20 mmol, 2.50 eq) were dissolved in ethyl acetate (8 mL). The solution was sonicated at ambient temperature for 4 h. The reaction mixture was washed with saturated sodium thiosulfate (2 × 20 mL) and water (20 mL), dried over sodium sulfate and filtered. The solvent was removed *in vacuo*. The product was obtained as an orange solid (577 mg, >99% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.03 (m, 2 H, Ar–H), 7.27–7.52 (m, 13 H, Ar–H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 148.8 (C═N), 141.0 (C–N), 140.5 (Ar–C), 132.3 (Ar–C), 130.7 (2 × Ar–C), 129.6 (Ar–C), 129.6 (2 × Ar–C), 129.2 (2 × Ar–C), 129.2 (Ar–C), 129.1 (2 × Ar–C), 129.1 (Ar–C), 129.0 (Ar–C), 128.4 (2 × Ar–C), 128.3 (Ar–C), 125.5 (C–Cl, Ar–C). Anal. Calcd for $C_{21}H_{15}BrN_2$·HCl: C, 68.68; H, 4.39; N, 7.63. Found: C, 68.66; H, 3.93; N 7.68. MS (ESI): m/z = 331 $[M + H]^+$.

5-Aminophenyl-3-methyl-1-phenyl-1*H*-pyrazole (14). 3-Methyl-1-phenyl-1*H*-pyrazol-5-one (**13**) (600 mg, 3.44 mmol, 1.00 eq), phosphorous pentoxide (293 mg, 2.06 mmol, 0.60 eq) and anilinium hydrochloride (535 mg, 4.13 mmol, 1.10 eq) were thoroughly mixed and irradiated in a microwave at 210 °C for 30 min. The black solid formed during the reaction was dissolved in water and ethanol (1 : 1, 10 mL). The aqueous phase was extracted with ethyl acetate (2 × 50 mL). The combined organic layers were dried over natrium sulfate, filtered and the solvent was evaporated *in vacuo*. Recrystallization of the residue from hexane–ethyl acetate yielded the product as a dark orange solid (522 mg, 64%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53–7.58 (m, 2 H, Ar–H), 7.44–7.59 (m, 2 H, Ar–H), 7.27–7.39 (m, 4 H, Ar–H), 6.59–7.00 (m, 2 H, Ar–H), 6.01 (s, 1 H), 5.63 (br, 1 H, NH), 2.35 (s, 3 H, CH_3). The analytical data was in accordance with the reported values.[23]

General procedure for the preparation of *trans*-dibromo-(1,3-diisopropylbenzimidazolin-2-ylidene)(pyrazole)palladium(II) complexes. The respective pyrazole (0.10 mmol, 2.0 eq) was added to a solution of di-μ-bromo-bis(1,3-diisopropylbenzimidazolin-2-ylidene)-dibromo-dipalladium(II) (**16**) (47 mg, 0.05 mmol, 1.0 eq) in dichloromethane (4 mL) and the resulting mixture was stirred at ambient temperature for 30 min. Then, the solvent was removed under reduced pressure and the remaining solid dried *in vacuo*.

***trans*-Dibromo(3,5-dimethyl-1-phenyl-1*H*-pyrazole)(1,3-diisopropylbenzimidazolin-2-ylidene)palladium(II) (17).** Complex **17** was prepared using 3,5-dimethyl-1-phenyl-1*H*-pyrazole (**5**) (17 mg, 0.10 mmol, 2.0 eq). 56 mg of a pale yellow solid were obtained (87% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.73–7.83 (m, 2 H, Ar–H), 7.56–7.71 (m, 3 H, Ar–H), 7.39–7.55 (m, 2 H, Ar–H), 7.08–7.18 (m, 2 H, Ar–H), 6.25 (sept, $^3J_{H–H}$ = 7.0 Hz, 1 H, C*H*$(CH_3)_2$), 6.08 (s, 1 H, CH), 5.27 (sept, $^3J_{H–H}$ = 7.0 Hz, 1 H, C*H*$(CH_3)_2$), 2.75 (s, 3 H, CH_3), 2.15 (s, 3 H, CH_3), 1.77 (d, $^3J_{H–H}$ = 7.0 Hz, 6 H, CH(C*H*$_3)_2$), 1.43 (d, $^3J_{H–H}$ = 7.0 Hz, 6 H, CH(C*H*$_3)_2$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 163.0 (NCN), 150.1 (N═C), 143.3 (N–C), 138.8 (Ar–C), 134.0 (Ar–C), 133.9 (Ar–C), 130.6 (2 × Ar–C), 129.7 (Ar–C), 129.4 (2 × Ar–C), 122.6 (2 × Ar–C), 113.1 (Ar–C), 113.0 (Ar–C), 108.0 (CH), 54.9 (*C*$(CH_3)_2$), 54.4 (*C*$(CH_3)_2$), 21.4 (C(*C*$H_3)_2$), 20.8 (C(*C*$H_3)_2$), 15.3 (CH_3), 12.7 (CH_3). Anal. Calcd for $C_{24}H_{30}Br_2N_4Pd$: C, 44.99; H, 4.72; N, 8.74. Found: C, 44.77; H, 4.58; N, 8.21. MS (ESI): m/z = 560 $[M - Br]^+$, 663 $[M + Na]^+$.

***trans*-Dibromo(1,3,5-triphenyl-1*H*-pyrazole)(1,3-diisopropylbenzimidazolin-2-ylidene)palladium(II) (18).** Complex **18** was prepared using 1,3,5-triphenyl-1*H*-pyrazole (**4**) (30 mg, 0.10 mmol, 2.0 eq). 73 mg of a pale yellow solid were obtained (95% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.41–8.48 (m, 2 H, Ar–H), 7.86–7.94 (m, 2 H, Ar–H), 7.56–7.63 (m, 5 H, Ar–H), 7.36–7.47 (m, 2 H, Ar–H), 7.22–7.31 (m, 5 H, Ar–H), 7.07–7.14 (m, 2 H, Ar–H), 6.76 (s, 1 H, CH), 5.93 (sept, $^3J_{H–H}$ = 7.0 Hz, 6 H, C*H*$(CH_3)_2$), 5.07 (sept, $^3J_{H–H}$ = 7.0 Hz, 6 H, C*H*$(CH_3)_2$), 1.55 (d, $^3J_{H–H}$ = 7.0 Hz, 6 H, CH(C*H*$_3)_2$), 1.41 (d, $^3J_{H–H}$ = 7.0 Hz, 6 H, CH(C*H*$_3)_2$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 161.6 (NCN), 147.9 (N–C), 154.9 (N═C), 139.4 (Ar–C), 134.0 (Ar–C), 133.9 (Ar–C), 133.2 (Ar–C), 131.6 (2 × Ar–C), 130.4 (2 × Ar–C), 129.9 (Ar–C), 129.6 (Ar–C), 129.5 (Ar–C), 129.4 (2 × Ar–C), 129.3 (Ar–C), 129.3 (2 × Ar–C), 129.1 (2 × Ar–C), 128.8 (2 × Ar–C), 122.6 (Ar–C), 122.5 (Ar–C), 113.0 (Ar–C), 113.0 (Ar–C), 107.8 (CH), 54.7 (*C*$(CH_3)_2$), 54.3 (*C*$(CH_3)_2$), 20.9 (C(*C*$H_3)_2$), 20.9 (C(*C*$H_3)_2$). Anal. Calcd for $C_{34}H_{34}Br_2N_4Pd$: C, 53.39; H, 4.48; N, 7.32. Found: C, 53.15; H, 4.27; N, 7.31.

***trans*-Dibromo(3,5-diisopropyl-1-phenyl-1*H*-pyrazole)(1,3-diisopropylbenzimidazolin-2-ylidene)palladium(II) (19).** Complex **19** was prepared using 3,5-diisopropyl-1-phenyl-1*H*-pyrazole (**6**) (23 mg, 0.10 mmol, 2.0 eq). 70 mg of a yellow solid were obtained (quantitative yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.75–7.83 (m, 2 H, Ar–H), 7.59–7.68 (m, 3 H, Ar–H), 7.46–7.53 (m, 1 H, Ar–H), 7.39–7.45 (m, 1 H, Ar–H), 7.08–7.16 (m, 2 H, Ar–H), 6.29 (sept, $^3J_{H–H}$ = 7.0 Hz, 6 H, C*H*$(CH_3)_2$), 6.09 (s, 1 H, CH), 5.10 (sept, $^3J_{H–H}$ = 7.0 Hz, 6 H, C*H*$(CH_3)_2$), 3.98 (sept, $^3J_{H–H}$ = 7.0 Hz, 6 H, C*H*$(CH_3)_2$), 2.77 (sept, $^3J_{H–H}$ = 7.0 Hz, 6 H, C*H*$(CH_3)_2$), 1.76 (d, $^3J_{H–H}$ = 7.0 Hz, 6 H, CH(C*H*$_3)_2$), 1.54 (d, $^3J_{H–H}$ = 7.0 Hz, 6 H, CH(C*H*$_3)_2$), 1.42 (d, $^3J_{H–H}$ = 7.0 Hz, 6 H, CH(C*H*$_3)_2$), 1.12 (d, $^3J_{H–H}$ = 7.0 Hz, 6 H, CH(C*H*$_3)_2$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 163.1 (NCN), 163.3 (C═N), 154.1, (C–N), 139.0 (Ar–C), 134.0 (Ar–C), 133.9 (Ar–C), 131.4 (2 × Ar–C), 129.8 (Ar–C), 129.3 (2 × Ar–C), 122.6 (Ar–C), 122.5 (Ar–C), 113.0 (Ar–C), 113.0 (Ar–C), 100.5 (CH), 54.9 (*C*$(CH_3)_2$), 54.3 (*C*$(CH_3)_2$), 29.1 (*C*$(CH_3)_2$), 26.4 (*C*$(CH_3)_2$), 23.4 (C(*C*$H_3)_2$), 23.1 (C(*C*$H_3)_2$), 21.3 (C(*C*$H_3)_2$), 20.9 (C(*C*$H_3)_2$). Anal. Calcd for $C_{28}H_{39}Br_2N_4Pd$: C, 48.26; H, 5.50; N, 8.04. Found: C, 48.48; H, 4.99; N 8.06.

***trans*-Dibromo(4-bromo-3,5-dimethyl-1-phenyl-1*H*-pyrazole)(1,3-diisopropylbenzimidazolin-2-ylidene)palladium(II) (20).** Complex **20** was prepared using 4-bromo-3,5-dimethyl-1-phenyl-1*H*-pyrazole (**8**) (25 mg, 0.10 mmol, 2.0 eq). 70 mg of a pale yellow solid were obtained (98% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61–7.82 (m, 5 H, Ar–H), 7.39–7.54 (m, 2 H, Ar–H),

7.08–7.18 (m, 2 H, Ar–H), 6.22 (sept, $^3J_{H-H}$ = 7.0 Hz, 1 H, C*H*-(CH_3)$_2$), 5.22 (sept, $^3J_{H-H}$ = 7.0 Hz, 1 H, C*H*(CH_3)$_2$), 2.76 (s, 3 H, CH_3), 2.17 (s, 3 H, CH_3), 1.77 (d, $^3J_{H-H}$ = 7.0 Hz, 6 H, CH(CH_3)$_2$), 1.42 (d, $^3J_{H-H}$ = 7.0 Hz, 6 H, CH(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 161.8 (NCN), 148.9 (N=C), 142.0 (N–C), 138.7 (Ar–C), 134.0 (Ar–C), 133.9 (Ar–C), 130.5 (2 × Ar–C), 130.2 (Ar–C), 129.6 (2 × Ar–C), 122.7 (2 × Ar–C), 113.1 (Ar–C), 113.0 (Ar–C), 97.2 (C–Br), 55.1 (C(CH_3)$_2$), 54.4 (C(CH_3)$_2$), 21.3 (C(CH_3)$_2$), 20.8 (C(CH_3)$_2$), 14.3 (CH_3), 12.1 (CH_3). Anal. Calcd for $C_{24}H_{29}Br_3N_4Pd{\cdot}CHCl_3$: C, 35.79; H, 3.60; N, 6.68. Found: C, 36.05; H, 3.18; N, 6.68. MS (ESI): m/z = 637 $[M - Br]^+$.

***trans*-Dibromo(4-iodo-3,5-dimethyl-1-phenyl-1*H*-pyrazole)(1,3-diisopropylbenzimidazolin-2-ylidene)palladium(II) (21).** Complex **21** was prepared using 4-iodo-3,5-dimethyl-1-phenyl-1*H*-pyrazole (**9**) (30 mg, 0.10 mmol, 2.0 eq). 79 mg of a pale yellow solid were obtained (quantitative yield). ^1H NMR (300 MHz, $CDCl_3$): δ 7.75–7.81 (m, 2 H, Ar–H), 7.62–7.71 (m, 3 H, Ar–H), 7.48–7.53 (m, 1 H, Ar–H), 7.41–7.46 (m, 1 H, Ar–H), 7.11–7.17 (m, 2 H, Ar–H), 6.22 (sept, $^3J_{H-H}$ = 7.0 Hz, 1 H, C*H*(CH_3)$_2$), 5.21 (sept, $^3J_{H-H}$ = 7.0 Hz, 1 H, C*H*(CH_3)$_2$), 2.78 (s, 3 H, CH_3), 2.20 (s, 3 H, CH_3), 1.77 (d, $^3J_{H-H}$ = 7.0 Hz, 6 H, CH(CH_3)$_2$), 1.43 (d, $^3J_{H-H}$ = 7.0 Hz, 6 H, CH(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 161.8 (NCN), 152.0 (N=C), 145.4 (N–C), 139.0 (Ar–C), 134.1 (Ar–C), 133.9 (Ar–C), 130.6 (2 × Ar–C), 130.2 (Ar–C), 129.6 (2 × Ar–C), 122.7 (2 × Ar–C), 113.2 (Ar–C), 113.0 (Ar–C), 65.9 (C–I), 55.1 (C(CH_3)$_2$), 54.5 (C(CH_3)$_2$), 21.4 (C(CH_3)$_2$), 20.9 (C(CH_3)$_2$), 16.2 (CH_3), 14.0 (CH_3). Anal. Calcd for $C_{24}H_{29}Br_2IN_4Pd{\cdot}CHCl_3$: C, 33.89; H, 3.41; N, 6.32. Found: C, 34.81; H, 3.19; N, 6.65. MS (ESI): m/z = 685 $[M - Br]^+$.

***trans*-Dibromo(4-chloro-1,3,5-triphenyl-1*H*-pyrazole)(1,3-diisopropylbenzimidazolin-2-ylidene)palladium(II) (22).** Complex **22** was prepared using 4-chloro-1,3,5-triphenyl-1*H*-pyrazole (**10**) (33 mg, 0.10 mmol, 2.0 eq). 80 mg of an orange solid were obtained (quantitative yield). ^1H NMR (300 MHz, $CDCl_3$): δ 8.26–8.35 (m, 2 H, Ar–H), 7.82–7.89 (m, 2 H, Ar–H), 7.53–7.70 (m, 6 H, Ar–H), 7.31–7.45 (m, 7 H, Ar–H), 7.06–7.14 (m, 2 H, Ar–H), 5.67 (sept, $^3J_{H-H}$ = 7.0 Hz, 6 H, C*H*-(CH_3)$_2$), 5.11 (sept, $^3J_{H-H}$ = 7.0 Hz, 6 H, C*H*(CH_3)$_2$), 1.50 (d, $^3J_{H-H}$ = 7.0 Hz, 6 H, CH(CH_3)$_2$), 1.41 (d, $^3J_{H-H}$ = 7.0 Hz, 6 H, CH(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 160.8 (NCN), 144.0 (N–C), 151.5 (C=N), 139.1 (Ar–C), 133.9 (Ar–C), 133.8 (Ar–C), 131.7 (2 × Ar–C), 131.3 (2 × Ar–C), 130.7 (Ar–C), 130.5 (2 × Ar–C), 130.1 (Ar–C), 130.1 (Ar–C), 129.8 (Ar–C), 129.4 (2 × Ar–C), 129.1 (2 × Ar–C), 128.7 (2 × Ar–C), 127.4 (Ar–C), 122.6 (Ar–C), 122.6 (Ar–C), 113.0 (Ar–C), 113.0 (Ar–C), 110.6 (C–Cl), 54.6 (C(CH_3)$_2$), 54.4 (C(CH_3)$_2$), 20.8 (C(CH_3)$_2$), 20.8 (C(CH_3)$_2$). Anal. Calcd for $C_{34}H_{33}Br_2ClN_4Pd$: C, 51.09; H, 4.16; N, 7.01. Found: C, 51.29; H, 4.45; N, 7.09.

***trans*-Dibromo(4-bromo-1,3,5-triphenyl-1*H*-pyrazole)(1,3-diisopropylbenzimidazolin-2-ylidene)palladium(II) (23).** Complex **23** was prepared using 4-bromo-1,3,5-triphenyl-1*H*-pyrazole (**11**) (38 mg, 0.10 mmol, 2.0 eq). 84 mg of an orange solid were obtained (quantitative yield). ^1H NMR (300 MHz, $CDCl_3$): δ 8.20–8.30 (m, 2 H, Ar–H), 7.81–7.88 (m, 2 H, Ar–H), 7.52–7.68 (m, 6 H, Ar–H), 7.32–7.44 (m, 7 H, Ar–H), 7.05–7.15 (m, 2 H, Ar–H), 5.61 (sept, $^3J_{H-H}$ = 7.0 Hz, 6 H, C*H*-(CH_3)$_2$), 5.10 (sept, $^3J_{H-H}$ = 7.0 Hz, 6 H, C*H*(CH_3)$_2$), 1.48 (d, $^3J_{H-H}$ = 7.0 Hz, 6 H, CH(CH_3)$_2$), 1.40 (d, $^3J_{H-H}$ = 7.0 Hz, 6 H, CH(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 160.8 (NCN), 152.9 (C=N), 145.7 (N–C), 139.1 (Ar–C), 133.9 (Ar–C), 133.8 (Ar–C), 131.9 (Ar–C), 131.4 (Ar–C), 131.2 (2 × Ar–C), 130.7 (2 × Ar–C), 130.3 (Ar–C), 130.1 (2 × Ar–C), 129.7 (Ar–C), 129.3 (2 × Ar–C), 129.0 (2 × Ar–C), 128.6 (2 × Ar–C), 128.0 (Ar–C), 122.6 (Ar–C), 122.6 (Ar–C), 113.0 (Ar–C), 113.0 (Ar–C), 96.8 (C–Br), 54.6 (C(CH_3)$_2$), 54.4 (C(CH_3)$_2$), 20.8 (C(CH_3)$_2$), 20.8 (C(CH_3)$_2$). Anal. Calcd for $C_{34}H_{33}Br_3N_4Pd$: C, 48.40; H, 3.94; N, 6.64. Found: C, 48.74; H, 4.16; N, 7.32.

***trans*-Dibromo(4-iodo-1,3,5-triphenyl-1*H*-pyrazole)(1,3-diisopropylbenzimidazolin-2-ylidene)palladium(II) (24).** Complex **24** was prepared using 4-iodo-1,3,5-triphenyl-1*H*-pyrazole (**12**) (42 mg, 0.10 mmol, 2.0 eq). 87 mg of an off-white solid were obtained (98% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 8.15–8.23 (m, 2 H, Ar–H), 7.84–7.86 (m, 2 H, Ar–H), 7.49–7.69 (m, 6 H, Ar–H), 7.31–7.45 (m, 7 H, Ar–H), 7.06–7.13 (m, 2 H, Ar–H), 5.55 (sept, $^3J_{H-H}$ = 7.0 Hz, 6 H, C*H*(CH_3)$_2$), 5.11 (sept, $^3J_{H-H}$ = 7.0 Hz, 6 H, C*H*(CH_3)$_2$), 1.47 (d, $^3J_{H-H}$ = 7.0 Hz, 6 H, CH(CH_3)$_2$), 1.40 (d, $^3J_{H-H}$ = 7.0 Hz, 6 H, CH(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 160.9 (NCN), 156.0 (N=C), 149.0 (N–C), 139.2 (Ar–C), 133.9 (Ar–C), 133.8 (Ar–C), 132.6 (Ar–C), 132.2 (2 × Ar–C), 131.1 (2 × Ar–C), 130.9 (2 × Ar–C), 130.1 (Ar–C), 130.0 (Ar–C), 129.7 (Ar–C), 129.3 (3 × Ar–C), 129.0 (2 × Ar–C), 128.6 (2 × Ar–C), 122.6 (Ar–C), 122.6 (Ar–C), 113.0 (Ar–C), 113.0 (Ar–C), 65.8 (C–I), 54.6 (C(CH_3)$_2$), 54.4 (C(CH_3)$_2$), 20.8 (C(CH_3)$_2$), 20.8 (C(CH_3)$_2$). Anal. Calcd for $C_{34}H_{33}Br_2IN_4Pd$: C, 45.84; H, 3.73; N, 6.29. Found: C, 45.93; H, 3.49; N, 6.57.

***trans*-Dibromo(5-methoxy-3-methyl-1-phenyl-1*H*-pyrazole)(1,3-diisopropylbenzimidazolin-2-ylidene)palladium(II) (25).** Complex **25** was prepared using 5-methoxy-3-methyl-1-phenyl-1*H*-pyrazole (**15**) (19 mg, 0.10 mmol, 2.0 eq). 66 mg of a yellow solid were obtained (quantitative yield). ^1H NMR (300 MHz, $CDCl_3$): δ 7.87–7.93 (m, 2 H, Ar–H), 7.59–7.66 (m, 2 H, Ar–H), 7.53–7.59 (m, 1 H, Ar–H), 7.48–7.53 (m, 1 H, Ar–H), 7.42–7.47 (m, 1 H, Ar–H), 7.11–7.16 (m, 2 H, Ar–H), 6.26 (sept, $^3J_{H-H}$ = 7.0 Hz, 6 H, C*H*(CH_3)$_2$), 5.60 (s, 1 H, CH), 5.43 (sept, $^3J_{H-H}$ = 7.0 Hz, 6 H, C*H*(CH_3)$_2$), 3.84 (s, 1 H, OCH_3), 2.76 (s, 1 H, CH_3), 1.77 (d, $^3J_{H-H}$ = 7.0 Hz, 6 H, CH(CH_3)$_2$), 1.45 (d, $^3J_{H-H}$ = 7.0 Hz, 6 H, CH(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 162.3 (NCN), 157.5 (N=C), 151.0 (N–C), 137.2 (Ar–C), 134.1 (Ar–C), 133.9 (Ar–C), 129.7 (2 × Ar–C), 129.4 (Ar–C), 129.2 (2 × Ar–C), 122.6 (2 × Ar–C), 113.0 (Ar–C), 113.0 (Ar–C), 87.8 (CH), 59.4 (OCH_3), 54.9 (C(CH_3)$_2$), 54.4 (C(CH_3)$_2$), 21.4 (C(CH_3)$_2$), 20.8 (C(CH_3)$_2$), 16.3 (CH_3). Anal. Calcd for $C_{24}H_{30}Br_2N_4OPd$: C, 43.89; H, 4.60; N, 8.53. Found: C, 43.61; H, 4.15; N, 8.85. MS (ESI): m/z = 616 $[M - Br]^+$.

***trans*-Dibromo(5-aminophenyl-3-methyl-1-phenyl-1*H*-pyrazole)-(1,3-diisopropyl-benzimidazolin-2-ylidene)palladium(II) (26).** Complex **26** was prepared using 5-aminophenyl-3-methyl-1-phenyl-1*H*-pyrazole (**14**) (25 mg, 0.10 mmol, 2.0 eq). 75 mg of a yellow solid were obtained (quantitative yield). ^1H NMR (300 MHz, $CDCl_3$): δ 7.88–7.93 (m, 2 H, Ar–H), 7.60–7.69 (m, 3 H, Ar–H), 7.47–7.52 (m, 1 H, Ar–H), 7.41–7.46 (m, 1 H, Ar–H),

7.20–7.29 (m, 2 H, Ar–H), 7.10–7.15 (m, 2 H, Ar–H), 6.94–7.00 (m, 3 H, Ar–H), 6.26 (sept, $^3J_{H-H}$ = 7.0 Hz, 1 H, C*H*-$(CH_3)_2$), 6.00 (s, 1 H, CH), 5.55 (s_{br}, 1 H, NH), 5.32 (sept, $^3J_{H-H}$ = 7.0 Hz, 1 H, C*H*$(CH_3)_2$), 2.75 (s, 3 H, CH_3), 1.78 (d, $^3J_{H-H}$ = 7.0 Hz, 6 H, CH(CH_3)$_2$), 1.44 (d, $^3J_{H-H}$ = 7.0 Hz, 6 H, CH(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ = 162.8 (NCN), 151.0 (C=N), 145.2 (C–N), 141.8 (C–N), 137.1 (Ar–C), 134.1 (Ar–C), 133.9 (Ar–C), 130.7 (Ar–C), 130.1 (Ar–C), 130.0 (2 × Ar–C), 129.9 (2 × Ar–C), 122.7 (Ar–C), 122.6 (2 × Ar–C), 117.9 (2 × Ar–C), 113.0 (Ar–C), 113.0 (Ar–C), 94.5 (CH), 54.9 (*C*$(CH_3)_2$), 54.4 (*C*$(CH_3)_2$), 21.4 (C(*C*H_3)$_2$), 20.8 (C(*C*H_3)$_2$), 15.9 (CH_3). Anal. Calcd for $C_{29}H_{33}Br_2N_5Pd$: C, 48.52; H, 4.63; N, 9.76. Found: C, 48.15; H, 3.93; N, 9.40. MS (ESI): m/z = 636 $[M - Br]^+$.

General procedure for the alkylation with bromoethane

The pyrazole was dissolved in bromoethane (2 mL) and the resulting mixture was heated to 45 °C for 3 d. Then, the solvent was removed under reduced pressure. The crude product was washed with diethyl ether and dried *in vacuo*.

General procedure for the alkylation with iodoethane

The pyrazole was dissolved in iodoethane (2 mL) and the resulting mixture was heated to 90 °C for 3 d. Then, the solvent was removed under reduced pressure. The crude product was washed with diethyl ether and dried *in vacuo*.

General procedure for the alkylation with trimethyloxonium tetrafluoroborate

Trimethyloxonium tetrafluoroborate (1.2 eq) was suspended in anhydrous dichloromethane (6 mL) under nitrogen atmosphere. The pyrazole was added, and the mixture was heated to reflux for 15 h. The solvent was removed *in vacuo*, the residue taken up in THF (0.5 mL), and the product was precipitated by addition of diethyl ether (~3 mL). It was isolated and dried *in vacuo*.

X-ray diffraction studies

X-ray data were collected with a Bruker AXS SMART APEX diffractometer, using Mo Kα radiation at 100(2) K (**21**·$CHCl_3$) or 223(2) K (**17**, **20**·$CHCl_3$ and **25**), with the SMART suite of programs.[24] Data were processed and corrected for Lorentz and polarisation effects with SAINT,[25] and for absorption effect with SADABS.[26] Structural solution and refinement were carried out with the SHELXTL suite of programs.[27] The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. All hydrogen atoms were put at calculated positions. All non-hydrogen atoms were generally given anisotropic displacement parameters in the final model. A summary of the most important crystallographic data is given in Tables 3 and 4.

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