CHEMISTRY
AN ASIAN JOURNAL
www.chemasianj.org

Accepted Article

Title: The forgotten nitro-aromatic phosphines as weakly donating P-ligands: a N-aryl-benzimidazolyl series in RhCl(CO) complexes

Authors: Chonhwei Zhu, Emmanuel Gras, Carine Duhayon, Francis Lacassin, Xiuling Cui, and Remi Chauvin

To be cited as: *Chem. Asian J.* 10.1002/asia.201701078

Link to VoR: http://dx.doi.org/10.1002/asia.201701078

A Journal of
ACES Asian Chemical Editorial Society

A sister journal of Angewandte Chemie and Chemistry – A European Journal

WILEY-VCH

10.1002/asia.201701078

The forgotten nitro-aromatic phosphines as weakly donating P- ligands: a N-aryl-benzimidazolyl series in RhCl(CO) complexes[†]

Chongwei Zhu,[a,b] Emmanuel Gras,[a,b]* Carine Duhayon,[a,b] Francis Lacassin,[a,b] Xiuling Cui,[c] Remi Chauvin[a,b,c] *

[a] *CNRS, LCC (Laboratoire de Chimie de Coordination), 205 route de Narbonne, BP44099, 31077 Toulouse Cedex 4 (France)*. Fax: (+33)5 61 55 30 03. E-mail: emmanuel.gras@lcc-toulouse.fr, *chauvin@lcc-toulouse.fr*

[b] *Université de Toulouse, UPS, ICT-FR 2599, 31062 Toulouse Cedex 9 (France)*

[c] *Engineering Research Center of Molecular Medicine, Ministry of Education, Key Laboratory of Xiamen Marine and Gene Drugs, Institutes of Molecular Medicine and School of Biomedical Sciences, Huaqiao University, Xiamen, 361021 (China).*

Keywords: benzimidazolophosphines, nitroarylphosphines, coordination bond, rhodium carbonyl complexes, nitro-aromatic chemistry

[†] This paper is dedicated to Prof. Marian Mikolajczyk on the occasion of his 80th birthday.

10.1002/asia.201701078

Abstract. The coordination chemistry of the *a priori* weakly σ-donating nitro-aromatic phosphines is addressed through a series of nitro-substituted (N-phenyl-benzimidazol-1-yl)diphenylphosphines in Rh(I) complexes. From a set of seven such phosphines L = $L_{xyz}^{(')}$ (x, y, z = 0 or 1 = number of NO_2 substituent at the 5, 6 and N-Ph *para* positions, respectively), including the non-nitrated parent L_{000} and its dicationic N-methyl counterpart L_{000}', three LRhCl(COD) and seven L_2RhCl(CO) complexes have been obtained in 72-95 % yield. Despite of a *cis* orientation of the L and CO ligands, the C=O IR stretching frequency ν_{CO} varies in the expected sense, from 1967 ± 1 cm^{-1} for L_{xy0} to 1978 ± 1 cm^{-1} for L_{xy1}, and 2005 cm^{-1} for L_{000}'. The ^{103}Rh NMR chemical shift δ_{Rh} varies from –288 ppm for L_{000} to –316 ± 1 ppm for L_{10z} or L_{01z}, and –436 ppm for L_{000}'. The ν_{CO} and δ_{Rh} probes thus reveal moderate but systematic variations, and act as "orthogonal" spectroscopic indicators of the presence of nitro groups on the N-Ph group and the benzimidazole core, respectively. For the dicationic ligand L_{000}', a tight electrostatic sandwiching of the Rh–Cl bond by the benzimidazole moities is evidenced by X-ray crystallography ($RhCl^{\delta-\cdots}CN_2^+$ ≈ 3.01 Å). Along with the LRhCl(CO) complexes, dinuclear side-products (μ-CO)$(RhClL)_2$ were also obtained in low spectroscopic yield: for the dinitro ligand L = $L_{011,}$ a unique 1:6.7 clathrate structure, with dichloromethane as solvate, is also revealed by X-ray crystallography.

1. Introduction

In the continuing debate on the fundamental nature of the coordination bond,[1] the ligands of some reference Lewis acid (LA) are commonly classified between the electron-rich and electron-poor categories: for transition metal LAs, this pre-bonding characteristic makes it possible to predict strong or weak ligand-to-metal charge transfer. Beside the long studied class of electron-rich ligands, ranging from alkylphosphines to diaminocarbenes and onium ylides,[2] the class of electron-poor phosphane counterparts has attracted less systematic attention but remains challenging for appraising coordination limits while decreasing the strength of σ-donation.[3] The need for electron-poor ligands is, however, more practically motivated by catalysis issues for rate-determining steps requiring a relatively low electron density at a metal center balanced by sufficient stability of the complex. Even weak, σ-donation can indeed be compensated by strong π-back bonding, as it happens with phosphites identified as ligands of choice for catalytic transformations such as hydroformylation.[4] As esters of phosphorous acid, phosphites are however sensitive to P–O bond protolysis, and two main kinds of more robust electron-deficient triarylphosphine ligands can be distinguished: the electron-poor neutral phosphines, mainly represented by fluoroarylphosphine,[5] N-heteroarylphosphines (e.g. imidazolophosphines),[6] and the *highly electron-poor* α-cationic phosphines, such as imidazolio-, diaminocyclopropenio-, or pyridinio-phosphines.[6a,7,8] These carbenio-phosphines, optimally described as carbene-phosphenium adducts,[9] have been shown to exhibit P-donating ability in ternary C→P→LA coordination motifs,[7a] even in the case of the *extremely electron-poor* α-diationic dicyclopropeniophosphines.[10] While cyclopropenio-phosphines give particularly stable Pd complexes acting as efficient catalysts (e.g. for enynes cyclo-isomerization),[7d,11] imidazolio-phosphines and their complexes are more reactive, undergoing P–C bond cleavage in the presence of weak nucleophiles (such as Cl^-), thus restricting the scope of possible applications.[9,12]

With the view to enhancing the electron-deficiency of the parent imidazolophosphines without the detrimental effect of the α-positive charge, N-methylation of the formers (CH_3^+ N-coordination) could be replaced by CH-substitution with neutral electron-withdrawing groups (Figure 1). Examination of this issue drew the authors' attention to the fact that an *a priori* simple way to make a triarylphosphine ligand more electron-deficient while remaining neutral seems to have been forgotten: alternative to fluorination, nitration should indeed be particularly efficient. Indeed, considering Hammett constants σ_p and σ_m as crude means of comparison of the electron-withdrawing effect of a substituent through an aromatic system,[13] one of the largest values is attained for NO_2 ($\sigma_m = 0.71$, $\sigma_p = 0.78$), standing close to that of the cationic substituent $^+NMe_3$ ($\sigma_m = 0.88$, $\sigma_p = 0.82$), and much higher than those of other neutral substituents such as F ($\sigma_m = 0.34$, $\sigma_p = 0.06$), CF_3 ($\sigma_m = 0.43$, $\sigma_p = 0.54$) or CN ($\sigma_m = 0.56$, $\sigma_p = 0.66$).[14]

Prior to any coordination chemistry considerations, the oxymoronic red-ox nature of nitro-substituted arylphosphines can be considered as a basic challenge,[15] at least from the thermodynamic standpoint (the nitro-nitroso isomerization 4-NO_2-C_6H_4-PPh_2→ 4-NO-C_6H_4-P(O)Ph_2 is calculated to be exothermic by ΔZPE = –23.2 kcal/mol; see SI).[16] Direct nitration of aryl-phosphines are prevented by the P-oxidizing potency of the nitronium ion,[17] and most of related synthetic efforts have focused on oxidized P=O or P=S precursors.[18] Coordination complexes of nitroarylphosphines are actually limited to the formal cases of such P→O or P→S derivatives: to the best of the authors' knowledge, indeed, no experimental example of corresponding P→metal complexes has ever been reported,[19] thus unveiling a quite general challenge. While the basic triphenylphosphine series will deserve a natural attention in particular for the reference (4-nitrophenyl)diphenylphosphine (see conclusion),[15b, 20] the forgotten nitration strategy for lowering further the electron deficiency of aromatic phosphine

ligands is hereafter addressed within the above-summarized concern in the benzimidazolyl phosphine series (Figure 1a).

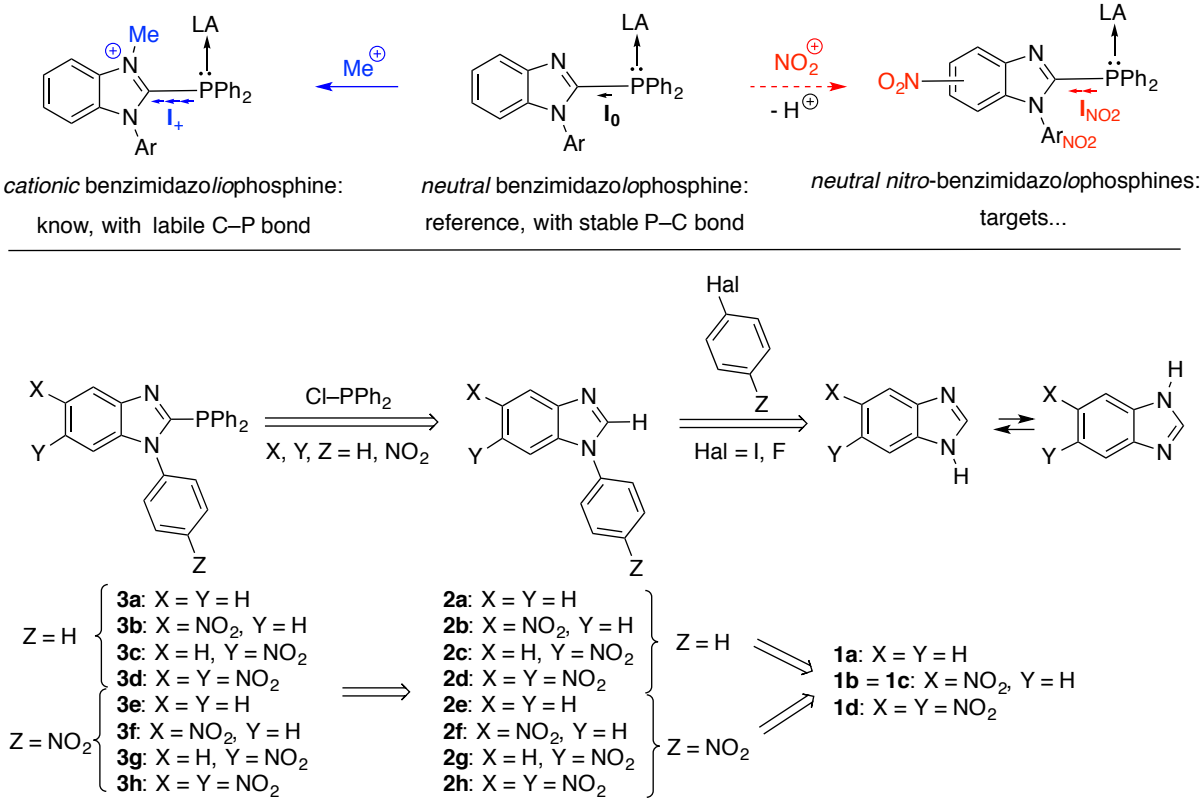


Figure 1. a) *top*: alternative manners to tune the P-σ-donating ability of benzimidazolophosphines towards a Lewis acid (LA): C-nitration *vs* N-alkylation (expected order of inductive effects: $\mathbf{I}_0 < \mathbf{I}_{NO2} < \mathbf{I}_+$); b) *bottom*: selected targets and synthetic approach.

While modern routes to arylphosphines consist in Cu-, Ni- or Pd-catalyzed Ar–P coupling reactions from Ar-X + E-PPh_2 (X = I, Br, OTf; E = H, Ph, $SnBu_3$, Cl), nitro-ArX substrates are rarely exemplified,[21] and have even been claimed to be incompatible with generally efficient conditions.[22] Yet, the most employed approach to tertiary phosphines remains based on nucleophilic substitution processes at P centers with lithium or Grignard reactants, as also illustrated in the arene/heteroarene series,[23] in particular for imidazole and benzimidazole representatives.[6e,12b] For the present objective, (*N*-aryl-*1H*-benzoimidazol-2-yl)diphenylphosphines have thus been targeted from the more or less nitrated *NH*,N_2*CH*

benzimidazole precursors **1a-d** by substitution of $ClPPh_2$ with lithium salts of *N-aryl*-N_2CH derivatives **2a-h** (Figure 1b). The propensity of nitro-arene/heteroarene substrates to undergo addition or redox processes in the presence of lithium reagents has indeed been reported for alkyl lithiums only.[24] Moreoever, since *N*-methyl-5-nitro-*1H*-benzoimidazol-2-yl lithium has been shown to undergo selective electrophilic chlorination with NCS,[25] reaction of the 1*N*-phenyl congener **2b** with the analogous Ph_2P–Cl electrophile appears as a natural possibility to prepare the set of eight more or less nitrated *N*-aryl-*1H*-benzoimidazolophosphines **3a-h** (Figure 1). Their coordinating properties were then envisaged to be compared by the ν_{CO} stretching frequencies of carbonyl complexes thereof (LA = $Ni(CO)_3$ in Figure 1a).[26] Instead of $Ni(CO)_3$ serving to define the Tolman's electronic parameters, LA = RhCl(CO) is here preferred for the sake of comparison with former results on related complexes of chelating bisimidazolophosphines,[27] and more generally because of the added value of the complementary ^{103}Rh NMR probe for rhodium-phosphine complexes.[28]

2. Results and Discussion

2.1. Synthesis of nitro-benzimidazolophosphines

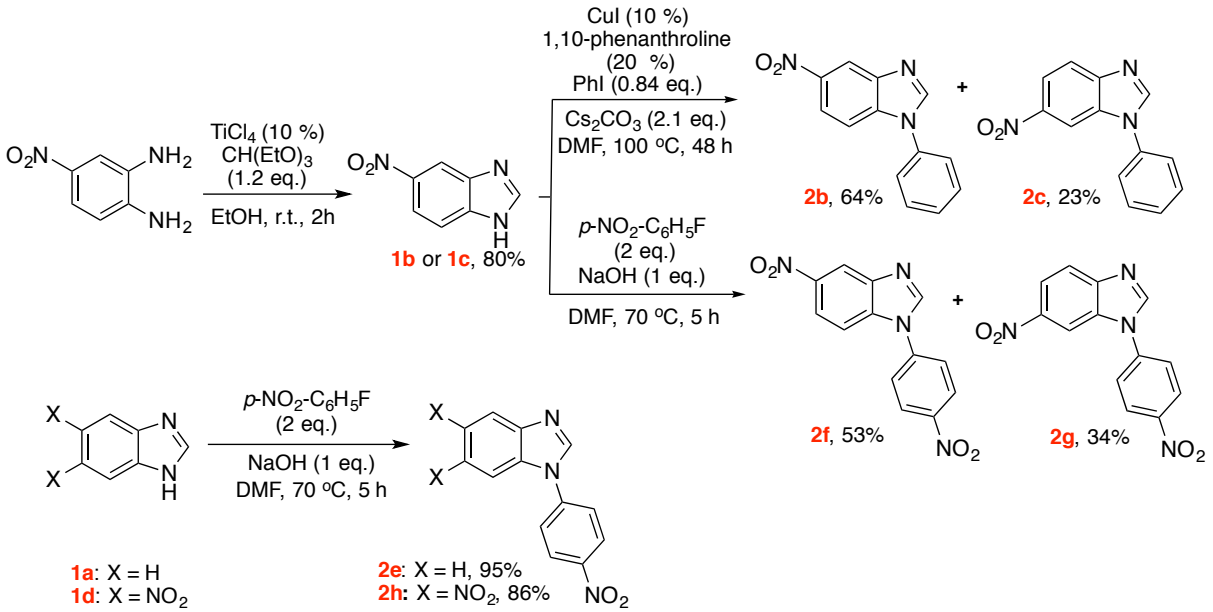
The four *NH*,N_2CH benzimidazole precursors **1a-d** were provided either as commercially available for **1a**, or prepared following known procedures; the nitro derivative **1b** or **1c** (in tautomeric equilibrium) was thus elaborated from 4-nitro-1,2-benzenediamine by condensation of triethylorthoester in the presence of a catalytic amount of $TiCl_4$ and the dinitro derivative **1d** was obtained by nitration of **1b-c** with fuming HNO_3 in concentrated H_2SO_4 (see experimental section 4.1 and cited references).

N-phenylation of **1a** and **1b-c** was implemented by copper-catalyzed C–N coupling from iodobenzene under conditions reported by Buchwald *et al.*,[29] yielding **2a** in 90 % yield,[30] and the isomers **2b** and **2c** in 64 % and 23 % yield, respectively, after separation by

10.1002/asia.201701078

column chromatography.[31] The method however failed to produce **2d** from **1d**, in correlation with the very low N-nucleophilicity of **1d** resulting from the cooperative effect of the two nitro groups.

N-*p*-nitrophenylation of **1a-c** was carried out by S_NAr of 4-fluoro-nitrobenzene, affording the known nitro derivative **2e** in 95 % yield,[30] and the isomers **2f** and **2g** in 53 % and 34 % yields, respectively.[32] Using the same procedure from **1d**, the trinitro derivative **2h** was isolated in 86 % yield.

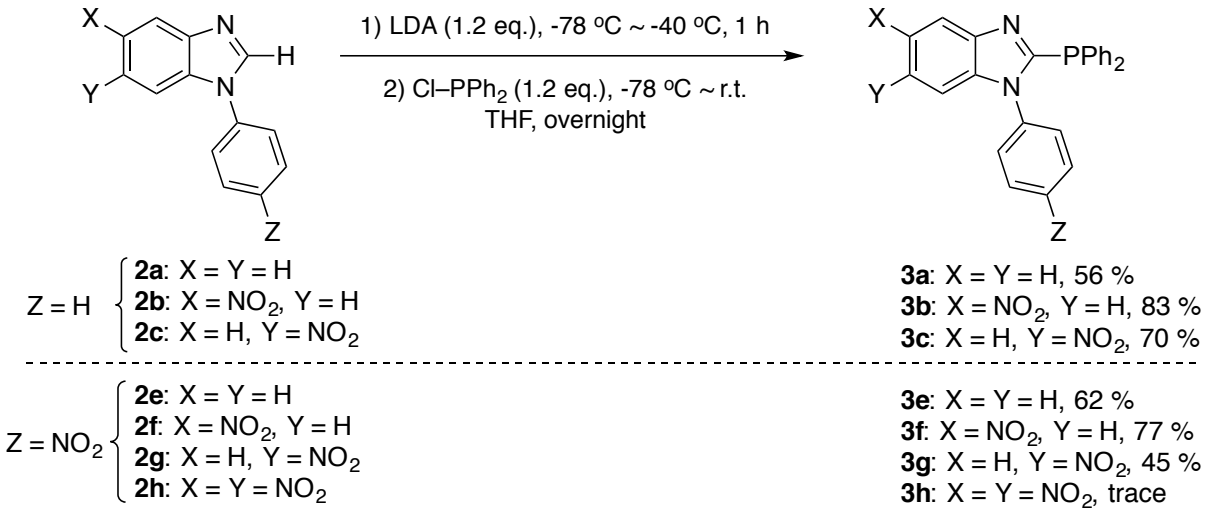


Scheme 1. Syntheses of nitro-functionalized benzimidazoles (for the 4,5-X_2 isomer of **1d**, **1d'**, see SI).

Phosphinylation of the lithium salts of **2a-c-2e-h** by nucleophilic substitution of $ClPPh_2$ required optimization of the initial deprotonation step. Inspired by the above-mentioned report on the selective deprotonation and reactivity of the N-methyl congener of **2b**,[25] the use of lithium diisopropylamide (LDA) as a base in THF was envisaged, with a strict control of the temperature at –78°C.[33] Applied to **2b**, these conditions indeed allowed isolation of **3b** in 83 % yield, in the absence of any oxyazobenzene side-product.[33] The same procedure gave access in 56 % yield to the reference non-nitrated benzimidazolophosphine

10.1002/asia.201701078

3a, previously reported to be available in 20 % yield only under metal free conditions (in the presence of NEt_3 as a base).[34] In a whole, application of the LDA procedure to **2a-c**-**2e-g** afforded **3a-c**-**3e-g** in 45-83 % yield, while only trace amounts of **3h** were obtained from the trinitro substrate **2h**. The phosphinylation selectivity was first evidenced by NMR spectroscopy by the disappearance of the amidine C^1H singlet signal at 8.10-8.90 ppm and the appearance of a $^{31}P\{^1H\}$ singlet signal in the range -21.3 / -24.5 ppm.



Scheme 2. Selective C-phosphinylation of nitro-functionalized benzimidazoles.

Single crystals of **3b**, **3c**, **3e** and **3f** deposited from solvent mixtures of pentane and dichloromethane (DCM) were found suitable for X-ray diffraction (XRD) analysis (see SI).[35] Notably, the structure of the 5-nitrobenzimidazolophosphine **3b** was resolved in the uncommon $P6_1$ space group of the hexagonal system. In all the structures, the C–P distances are virtually identical (1.83 ± 0.01 Å) and the torsion angles between the N–Ar and benzimidazole mean planes have a median value of 68.5 ± 1.3°. The amidine sp^2-C1 atom is found slightly pyramidalized, with a tilting angle of the C–P bond axis *vs* the imidazole ring mean plane of *ca* 4.7 ± 0.3° for **3c** and **3e-f**, but reaching 11.3° for **3b**.

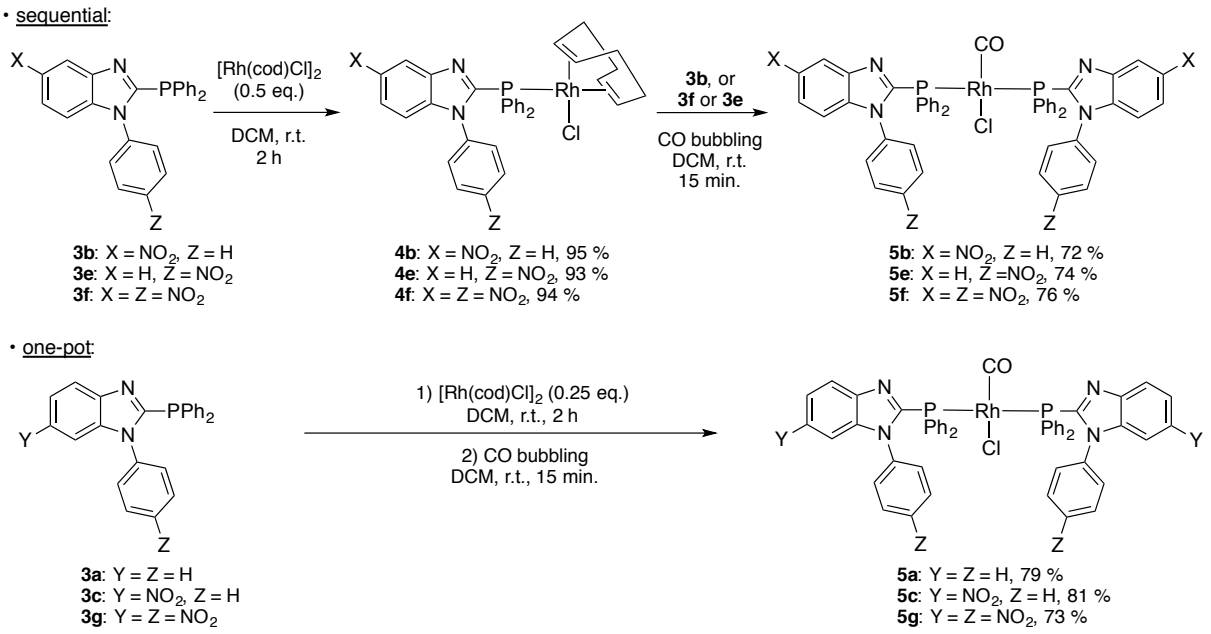
10.1002/asia.201701078

2.2. Coordination complexes of nitro-benzimidazolophosphines

With the view to comparing the coordinating properties of the benzimidazolophosphines through IR ν_{CO} values of RhCl(CO) complexes of type **4** (Scheme 3), **3a-c** and **3e-h** were first sequentially reacted with $[Rh(COD)Cl]_2$ (for cleavage of the μ-Cl bridges; COD = 1,5-cyclooctadiene) before displacement of the COD ligand by a second equivalent of the phosphine and a carbonyl ligand.

Reaction of **3b** with half an equivalent of $[Rh(COD)Cl]_2$ in DCM for 2 h at room temperature led to the COD complex **4b** in 95 % yield. P-Rh coordination was established by the change of the $^{31}P\{^1H\}$ NMR signal, shifting from -22.88 to +19.00 ppm, and splitting from a singlet to a doublet with a coupling constant of 150.7 Hz characteristic of a $^1J_{PRh}$ coupling. Moving the nitro group from the benzimidazole core in **3b** to the Ar N-substituent in **3e** did not alter the reactivity with the Rh(I) dimer, giving **4e** in 93 % yield. Likewise, reaction of the dinitro benzimidazolophosphine **3f** with $[Rh(COD)Cl]_2$ gave **4f** in a similar 94 % yield. Further displacement of the COD ligand of **4b**, **4e** and **4f** was achieved by adding one additional equivalent of the respective phosphines **3b**, **3e** and **3f**, followed by CO bubbling for 15 min, thus affording the diphosphine RhCl(CO) complexes **5b**, **5e** and **5f** in 74 ± 2 % yield (Scheme 3). In each case, another phosphine-rhodium complex numbered as **6b**, **6e** or **6f** was concomitantly formed as an initially non-identified side-product, the structural assignment of which could be achieved by crystallographic analysis only (see section 2.4, Figure 3).

10.1002/asia.201701078



Scheme 3. Sequential and one-pot two-step syntheses of RhCl(CO) complexes of nitro-substituted benzimidazolophosphines. From **6x**, an initially non-identified side products respectively denoted as **6x** (**x** = **b-c e-g**) were also obtained (see Figure 3, section 2.4).

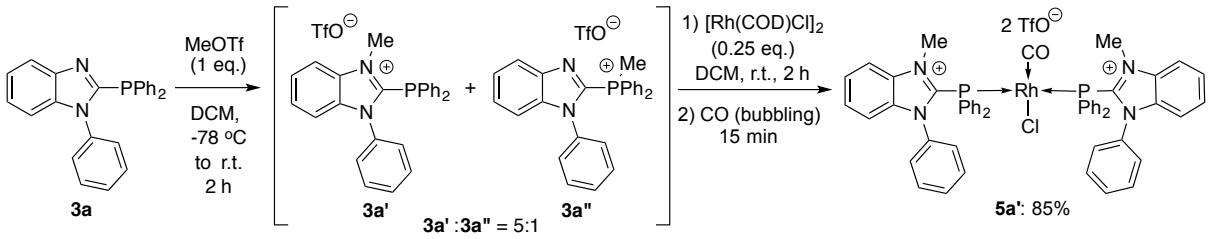
A one-pot procedure was also attempted, providing the target complexes with slightly higher overall yields, as illustrated from **3a**, **3c** and **3g** (Scheme 3). Two equivalents of **3c** were thus treated with half an equivalent of $[Rh(COD)Cl]_2$ in DCM for 2 h at r.t., and subsequently with bubbling carbon monoxide for 15 min., affording **5c** in 81 % yield. The same treatment from **3a** and **3g** providing directly **5a** and **5g** in 79 % and 73 % yield, respectively. In all cases involving a nitro ligand (not in the case of **5a**), the side-product of initially unknown structure **6x** (**x** = **b-c**, **e-g**) was also observed (see section 2.4).

For the sake of reference to the original concern, the RhCl(CO) complex **5a'** of the cationic benzimidaz*olio*phosphine **3a'** was also targeted. Treatment of **3a** with one equivalent of methyl triflate (MeOTf) in DCM at -78°C actually led to the *N*-methylated target product **3a'** in mixture with the *P*-methylated isomer **3a''** in a 5:1 ratio, as evidenced by the disappearance of the ^{31}P NMR signal of **3a** (-24.49 ppm) and appearance of two signals at –

10.1002/asia.201701078

15.48 and +14.36 ppm consistent with the structures of **3a'** and **3a"**, respectively. This lack of N/P selectivity in the reaction of the hard methylating agent MeOTf with imidazolophosphine is unprecedented, but correlated with the absence of a second P center in the monophosphine **3a** as compared to the cases of the *N*-aryl benzimidazolo- and imidazolo-diphosphines BIMINAP (2-(diphenylphosphanyl)-1-[2-(diphenylphosphanyl)naphthalen-1-yl]-1*H*-1,3-benzodiazole) and BIPHIMIP (2-(diphenylphosphanyl)-1-[2-(diphenylphosphanyl)phenyl-1*H*-imidazole).[6e,12b, 36] Under the same conditions, treatment of the 5-nitrobenzimidazolophosphine **3b** with MeOTf gave a mixture of the *N*- and *P*-methylated isomers **3b'** and **3b"** in a 3:2 ratio according (see SI): this further lowering of N/P selectivity can be interpreted by the electron-withdrawing effect of the nitro group decreasing the electron density of the N atom more than that of the more remote P atom.

As the two cations **3a'** and **3a"** could not be efficiently separated, the 5:1 mixture was used in coordination experiments. Treatment of this mixture with 0.25 mol. equivalent of $[Rh(COD)Cl]_2$ with respect to **3a'**, before bubbling carbon monoxide for 15 min. allowed the complex **5a'** to be isolated in a high 85 % yield after removal of **3a"** by washing the DCM-containing residue with cold pentane.



Scheme 4. *N- vs P*-methylation of the benzimidaz*olo*phosphine **3a**, and P-coordination of the benzimidaz*olio*phosphine product **3a'** at a RhCl(CO) center.

The $P_2RhCl(CO)$ complexes of type **5** have been characterized by ^{1}H, ^{13}C, ^{31}P and ^{103}Rh NMR and IR spectroscopy (see section 2.3). Remarkably, no MS method, among ESI,

APCI and MALDI, was found suitable to produce molecular peaks of the complexes, preventing structural confirmation by HRMS: the lability of primary cationic species generated in the MS chamber is actually correlated with the weak donating ability of the monodentate ligands. The structures of **5a-c**, **5f-g** and **5a'** were more precisely determined by XRD analysis of single crystals grown slowly from DCM solutions (Table 1, Figure 2). Notably, the structure of the dinitro ligand complex **5f** was resolved with the chiral space group $P2_12_12_1$. In the crystal state, all the complexes were found to exhibit a square planar-like geometry, with a *trans* arrangement of the two phosphine ligands, and an occupation disorder of the facing Cl and CO ligands, except for **5f** and **5a'**. While the Rh-Cl and Rh–C distances vary in the ranges 2.38 ± 0.03 Å and 1.81 ± 0.02 Å, respectively, the C–P distances remain close to 2.31 ± 0.01 Å. The C-O distance, varying in the range 1.14 ± 0.03 Å (Table 1), appears not to be a significant indicator of the global electron-donating ability of the phosphine ligand.[37a] This can be ascribed to the *cis*-orientation of the P–Rh–CO bonds, and to the long recognized considerably weaker geometrical *cis*-influence of a P ligand on the lengthening of a geminal Rh–L bond (with an even weaker correlated influence on the C=O bond length for L = CO) as compared to the corresponding *trans*-influences.[37b] For the *a priori* least donating dicationic ligand **3a'**, the intermediate C-O distance value of 1.14 Å is, however, also correlated with the unique conformational features of the complex **5a'**. In the neutral complexes **5a-c**, **5f-g**, indeed, the $ImPh_2P$–(Rh)–PPh_2Im unit adopts a staggered conformation, with perfectly anti-periplanar imidazolyl groups in **5a-c** and **5g** (Im–P–P–Im dihedral angles = 180°), and synclinal-gauche imidazolyl groups wrapping the Rh–Cl bond in **5f** (Im–P···P–Im dihedral angle = 45°, N_2C…Cl ≈ 3.28 Å). In contrast, the dicationic complex **5a'** exhibits a perfectly eclipsed conformation of Rh–Cl bond with both the *syn*-periplanar imidazolyl groups (Im–P···P–Im dihedral angle = 2.8°); the shortness of the $N_2C^{+}\cdots Cl^{\delta-}$ distances (3.01 ± 0.01 Å) is attributed to the electrostatic effect.

10.1002/asia.201701078

Table 1. Crystallographic data for the complexes **5a-c**, **5f-g** and **5a'**.

	5a	**5b**	**5c**	**5f**	**5g**	**5a'**	**6f**
CCDC no	1496162	1496160	1496161	1496163	1496164	1496165	1496166
Empirical formula	$C_{51}H_{38}Cl$ N_4OP_2Rh	$C_{55}H_{44}Cl_9$ $N_6O_5P_2Rh$	$C_{51}H_{36}Cl$ $N_6O_5P_2Rh$	$C_{53}H_{38}Cl_5$ $N_8O_9P_2Rh$	$C_{53}H_{38}Cl_5$ $N_8O_9P_2Rh$	$C_{58.5}H_{51}Cl_8F_6$ $N_4O_7P_2RhS_2$	$C_{57.7}H_{47.4}Cl_{15.4}$ $N_8O_9P_2Rh_2$
M_r	923.19	1352.92	1013.19	1273.05	1273.05	1548.67	1810.59
Cryst. system	monoclinic	triclinic	triclinic	orthorhombic	orthorhombic	triclinic	triclinic
Space group	$P2_1/n$	P-1	P-1	$P2_12_12_1$	$Pbca$	P-1	P-1
T [K]	100	100	100	100	120	100	100
a [Å]	10.704(3)	9.5819(3)	8.8037(4)	14.0668(9)	15.9457(5)	14.7172(11)	10.5619(3)
b [Å]	11.496(4)	10.7141(4)	10.9560(6)	16.7870(13)	11.2917(3)	15.0289(11)	17.8643(6)
c [Å]	17.080(4)	14.7256(6)	12.0990(6)	22.524(2)	29.2082(11)	18.4532(14)	19.6796(7)
α [°]	90	98.0370(16)	87.651(2)	90	90	91.977(3)	97.7610(16)
β [°]	99.466(9)	102.8561(16)	79.310(2)	90	90	109.881(2)	90.9492(15)
γ [°]	90	102.9773(16)	69.853(2)	90	90	117.436(2)	104.4739(14)
V [Å^3]	2073.1(5)	1407.26(6)	1076.24(9)	5318.8(5)	5259.08(19)	3316.0(4)	3557.48(13)
D_c	1.479	1.596	1.563	1.590	1.608	1.551	1.690
Z	2	1	1	4	4	2	2
μ(MoKα) [mm^{-1}]	0.599	0.842	0.593	0.698	0.706	0.761	1.146
Refl. measured	31654	86814	52472	79662	76783	106296	180292
Refl. unique/R_{int}	4800/0.143	12318/0.026	4759/0.038	13763/0.058	7694/0.098	21412/0.030	24511/0.035
Refl. [$I > 3\sigma(I)$]	2792	10661	4427	11405	4876	16438	18966
Nb parameters	274	403	313	704	352	811	928
R	0.0560	0.0389	0.0266	0.0309	0.0621	0.0560	0.0348
R_w	0.0609	0.0348	0.0233	0.0312	0.0751	0.0540	0.0366
S = GooF	1.121	1.049	1.073	1.093	0.999	1.030	1.077
$\Delta\rho_{max}/\Delta\rho_{min}$ [e.Å^{-3}]	1.20/-1.99	0.98/-0.67	0.41/-0.72	0.57/-0.41	0.95/-1.03	2.40/-0.96	2.10/-1.27

10.1002/asia.201701078

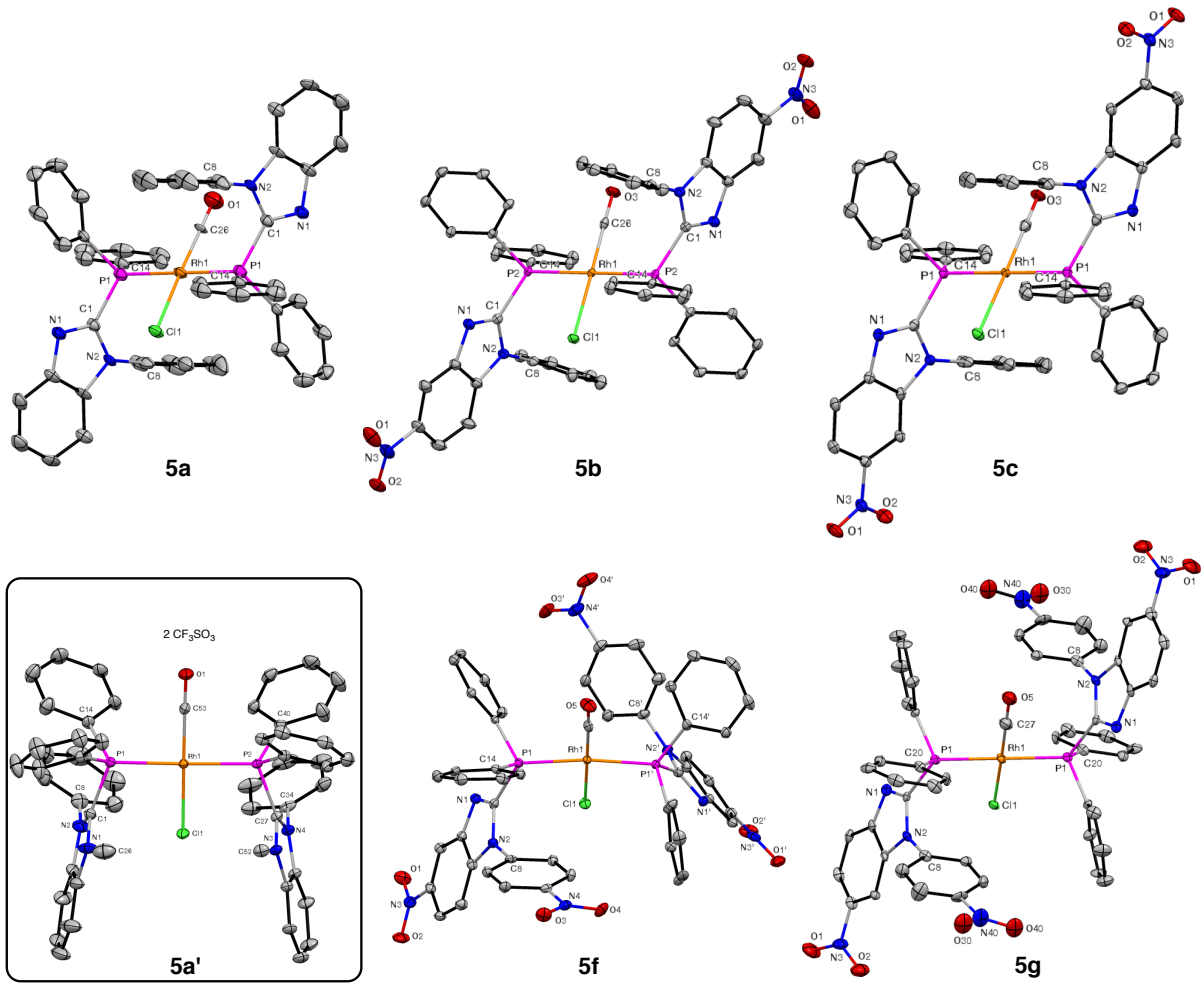


Figure 2. XRD molecular views of **5a-c**, **5f-g** and **5a'** (see section 4.4). Thermal ellipsoids at the 50 % probability level. For clarity, hydrogen atoms are omitted. The ellipsoid diagrams of the triflate anions of **5a'** are also omitted. The N-Ph and P-Ph *ipso* atoms reveal a π-stacking interaction: C8-C14 ≈ 3.26 Å (**5a**), 3.20 Å (**5b**, **5c**), 3.18 Å (**5f**), 3.14 Å (**5a'**); C8-C20 ≈ 2.24 Å (**5g**); C34-C40 ≈ 3.14 Å (**5a'**). In the dication **5a'**, the sandwiching of the Cl atom by the benzimidazolium moieties is indicated by the short distances: Cl1-C1 ≈ Cl1-C27 = 3.01 ± 0.01 Å, Cl1-N1 ≈ Cl1-N3 = 3.20 Å, Cl1-N2 ≈ Cl1-N4 = 3.41 ± 0.00 Å Cl1-C26 ≈ Cl1-C52 = 3.55 ± 0.05 Å.

10.1002/asia.201701078

2.3. Tentative analysis of coordination properties of nitro-benzimidaz*olo*phosphines

Disregarding the classical broadness of the ^{1}H signals of the cycloctadiene ligand in complexes **4**, all the other signals of NMR spectra of complexes **4** and **5** recorded at room temperature are particularly sharp (see SI, section 2, pp. 32-51), ruling out any slow equilibrium between a main *trans* form (found in the crystal state) and significant proportion of the putative *cis* isomer. The latter is indeed expected to be thermodynamically highly disfavored by the bulkiness of the P environment. Notably, the ^{31}P coordination shift $\Delta\delta_{31P}$(**x**) = δ_{31P}(**5x**) – δ_{31P}(**3x**) (**x** = **a-g**, **a'**) is found larger for the cationic ligand ($\Delta\delta_{31P}$(**a'**) = 53.6 ppm) than for the neutral ligands, for which $\Delta\delta_{31P}$ is found to depend on the presence of NO_2 groups on the benzimidazole core only (Table 2): $\Delta\delta_{31P}$ ≈ 45.5 ± 0.1 ppm for a non-nitrated benzimidazole core (**x** = **a**, **e**), $\Delta\delta_{31P}$ ≈ 46.6 ± 0.3 ppm otherwise (**x** = **b**, **c**, **f**, **g**). At last, the $^{1}J_{RhP}$ coupling constant does not vary significantly remaining in the range 129.6 ± 1.5 Hz for all the neutral complexes, and just reaching 132.8 Hz for the dicationic complex **5a'**.

In a more classical approach, the IR stretching frequency of the CO co-ligand (ν_{CO}) and ^{103}Rh, ^{31}P NMR chemical shifts (δ_{103Rh}, δ_{31P}(**5x**)) of the (**3x**)$_2$RhCl(CO) complexes **5x** in CD_2Cl_2 solutions were selected for appraising the coordinating properties of **3x**, **x** = **a-g**, **a'** (Table 2). The "pre-coordinating" properties of the latter was also tentatively envisaged to be revealed by its ^{31}P NMR chemical shift in the free state, δ_{31P}(**3x**).

10.1002/asia.201701078

Table 2. Selected IR, NMR spectroscopic or crystallographic data for the ligands **3a-c**, **3f-g**, **3a'** or complexes thereof.[a,b)]

charge	Z	x[a)]	ν_{CO} (**5x**)[c)] (cm^{-1})	$\delta 103_{Rh}$ (**5x**)[f)] [d)](ppm)[e)]	δ_{31P} (**5x**) (ppm)	$\Delta\delta_{31P}$(**x**)[g)] (ppm)	$^1J_{RhP}$ (Hz)	δ_{31P} (**3x**) (ppm)	δ_{31P} (**3xO**) (ppm)	$d_{C\text{-}O}$ (**5x**)[h)] (Å)
0	H	**a**	1966	- 8586 -288	20.9	45.4	129.6	-24.5	17.0	1.110(14)
0	H	**b**	1968	-8613 -316	23.7	46.7	129.6	-23.0	17.6	1.138(4)
0	H	**c**	1969	-8612 -315	23.9	46.4	131.2	-22.5	17.4	1.160(5)
0	NO_2	**e**	1979	n.d.	22.3	45.7	128.3	-23.4	18.1	-
0	NO_2	**f**	1978	n.d.	25.0	46.9	129.6	-21.9	17.9	1.157(3)
0	NO_2	**g**	1980	- 8612 -315	25.0	46.3	129.6	-21.3	17.9	1.161(16)
+1	H	**a'**	2005	- 8733 -436	38.1	53.6	132.8	-15.5	-	1.141(3)

a) Substitution pattern (**x** = **a**-**g**, **a'**) of N-phenyl-benzimidazole core as defined in Figure 1 (X, Y, Z = H, NO_2) and Scheme 4 (for **a'**). b) NMR spectra of solutions in CD_2Cl_2 (see SI); c) from IR spectra in the solid state recorded by the ATR (attenuated total reflection) technique; d) chemical shift with respect $Rh(acac)_3$ with the frequency ratio Ξ' = 3.186447 % of (see section 4.3); e) chemical shift for the formal frequency ratio Ξ = 3.160000 % (see section 4.3); f) the $^1J_{Rh\text{-}P}$ coupling constants remain similar, varying from 128.3 Hz for **5e** to 132.8 Hz for **5a'**; g) coordination shift: $\Delta\delta_{31P}$(**x**) = δ_{31P}(**5x**) – δ_{31P}(**3x**); h) from X-ray diffraction data (see Table 2 and SI).

As previously observed in related RhX(COD)(phosphine) complexes,[38] no correlation is observed between δ_{103Rh}(**5x**) and either δ_{31P}(**5x**) or δ_{31P}(**3x**). P-coordination to non-metal hard Lewis acids such an oxygen atom is the singlet spin state (promoted oxygen, O*) was also envisaged in the corresponding phosphine oxides **3xO**, **x** = **a**-**g**, generated by treatment of **3x** with H_2O_2 (**3aO** and **3bO** were also isolated and characterized: see SI); the ^{31}P NMR shifts of **3xO** remain however almost constant at 17.5 ± 05 ppm.

The ν_{CO} and $\delta_{^{103}Rh}$ parameters thus appear to play complementary roles for appraising the effects of nitro substituents on either the benzimidazole core or pending N-phenyl group, respectively.

Whatever the nitro-decoration of the benzimidazole core, indeed, a N-phenylated ligand gives ν_{CO} = 1968 ± 1 cm^{-1} (**5a-c**) and a N-*p*-nitrophenylated ligand gives ν_{CO} = 1979 ± 1 cm^{-1} (**5e-g**). Using the ^{103}Rh NMR probe (see section 4.3), whatever the N-aryl substituent, the presence of a nitro substituent on the benzimidazole core (at either position 5 or 6) gives $\delta_{^{103}Rh}$ = –315 ppm, *vs* $\delta_{^{103}Rh}$ = –288 ppm for the non-nitrated reference **5a** (the value for **5e** could however not be determined due to solubility issues). The ν_{CO} and $\delta_{^{103}Rh}$ values for the dicationic complex **5a'** are out of range, but relatively consistent with the expected effects of "electronegative" substituents on the global donating character of the P atom towards the RhCl(CO) center.

The sensitivity of the ν_{CO} value to *p*-nitro-substitution at the N-phenyl group is remarkable (+10 cm^{-1} for a remote NO_2 group, nine-bond away from the CO ligands), in particular with regard to the vanishing effect of nitro substitution at the benzimidazole core in spite of π-conjugation with the coordinating P center. Whatever the electronic process at stake (partial π-conjugation and/or σ-inductive attraction through the N–Ar bond), the observation is in line with former observations of a marked effect of N-nitroaryl and N-fluoroaryl substitution on intrinsic π-accepting ability or catalytic properties of imidazol-2-ylidene ligands.[39]

2.4. Dinuclear nitro-benzimidazolophosphine side products: CH_2Cl_2-clathrate complexes

Each of the nitro-containing complexes **5b-c**, **5e-g** (Scheme 3) was actually obtained in mixture with a side product containing a Rh–P bond, as evidenced by ^{31}P NMR spectroscopy of the crude material, and denoted as **6b-c**, **6e-g** (see experimental section 4.2). The exact

structure of theses complexes could however not be assessed by spectroscopic methods. In the case of the dinitro ligand **3f**, however, crystals of **6f** deposited from a DCM solution of the residue obtained from the supernatant of crystals of **5f** after reaction of **3f** with **4f** (Scheme 3). X-ray diffraction analysis showed a dinuclear structure, where the two Rh centers are in distorted bipyramidal environments, coordinated by a μ-CO and two P,N-bridging ligands **3f** (Figure 3). The corresponding structures are assigned to the side-products **6b**, **6c**, **6e** and **6g** obtained from **4b**, **4c**, **4e** and **4g**, respectively.

A search in the CCDC database for similar complexes featuring such a $[Rh_2(\mu\text{-}CO)Cl_2]$ core gave 18 related examples, five of them featuring P,N coordination to the Rh centers, with Rh-Rh bonding distances ranging from 2.57 Å to 3.01 Å.[40] The Rh–Rh distance of 2.63 Å measured in **6f** is thus quite short, smaller than the average value of 2.68 Å over the series. The Rh–Cl bonds of **6f** (bent from the Rh–Rh axis by *ca* 163°) are significantly shorter than all the corresponding bonds within the CCDC sampling (2.36 Å *vs* 2.42 to 2.45 Å). The C–O distance of 1.17 Å measured in **6f** is identical to the average value over the CCDC series. The Rh–P bonds of **6f** are found quite short (2.21-2.22 Å), and much shorter than in the parent complex **5f** (2.31 Å). The Rh–N bonds are however found consistently shorter (2.08-2.10 Å).

The crystals of **6f** are actually clathrates, with 6.7 DCM molecules *per* molecule of **6f**. The high solvent content was actually first suspected after observing disintegration of isolated crystals in polyisobutene blend oils used as cryo-protectants for XRD analysis (PARATONE or PARABAR 10312; the use of a perfluoropolyether oil, PFO-XR 75, was finally required). The solvate molecules are spread over 12 positions, eight of them being partially occupied and forming a chain with short distances between positions strongly occupied by Cl atoms (Cl…Cl ≈ 3.5 Å), thus suggesting that the chain cohesion is due to halogen bonding,[41a] today widely invoked in crystal engineering.[41b-c] Chains of DCM molecules were also proposed to

10.1002/asia.201701078

occur in a related dirhodium complex,[40i] but the extended van des Waals gallery within the crystal network of **6f** (Figure 3) meets more general challenges in the search for metal-organic inclusion compounds of the clathrate type or porous coordination polymers,[42a] in particular for DCM guest molecules which are more currently found hosted by organic lattices.[42b-e] Within the family of the Werner clathrates, based on a discrete packing of MX_2L_4 complexes (M = divalent transition metal ion, X = small anionic ligand, L = pyridine ligand),[42f] and related Hoffmann clathrates based on a grid of CN-bridged coordination polymer (initiated by the cadmium(II)-CCl_4 clathrate),[42g-h] one may cite the Werner DCM-clathrate $[Ni(NCS)_2(3\text{-cyanopyridine})_4]\bullet 2CH_2Cl_2$.[42i] More particular examples are the recently described dinuclear clathrates $[Cd_2I_2(\mu\text{-}L)_2]\bullet CH_2Cl_2$ (L = 4,4'-bis(2-methylimidazol-1-ylmethyl)biphenyl),[42j] and $[Ag(NO_3)_2Pt(\mu\text{-}$ benzothiadiazol-4-ylethynyl)(4-diphenylaminopyridine)$]\bullet CH_2Cl_2$,.[42k]

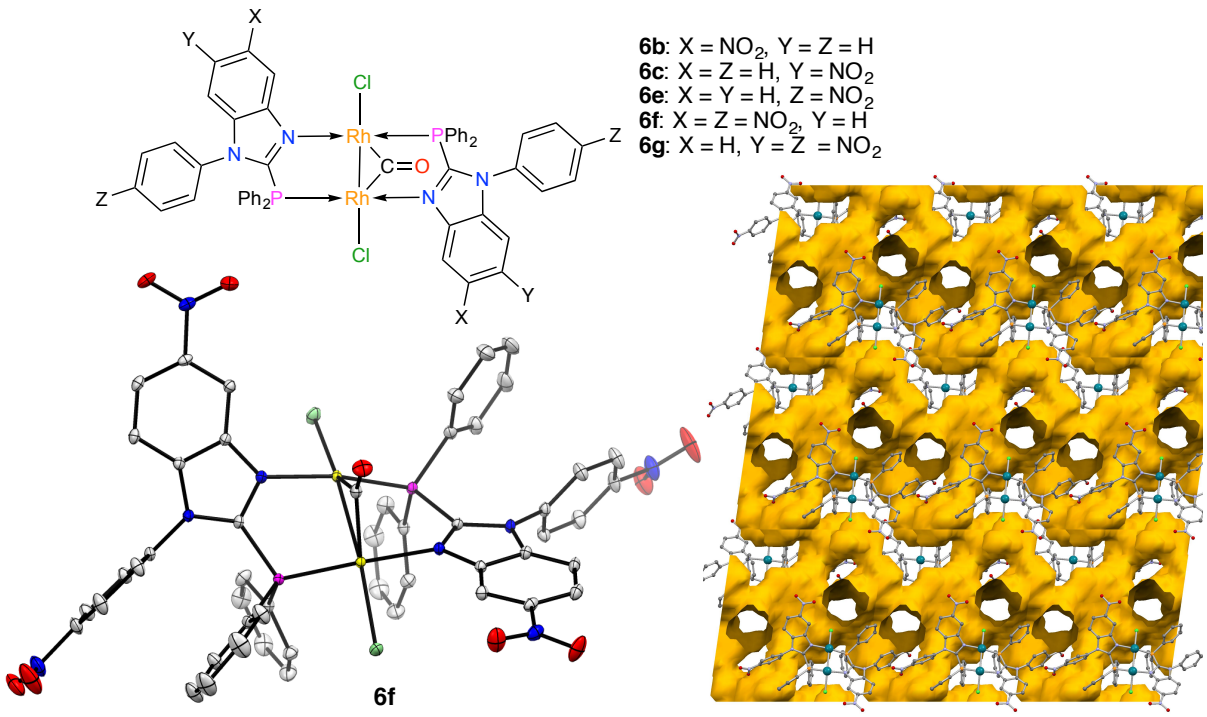


Figure 3. Lewis structure of the dinuclear side-products formed along with the target complexes **5b-c**, **5e-g** (Scheme 3; *top*), crystallographic molecular view of **6f** with thermal ellipsoids at the 50 % probability level (*bottom left*), and free van der Waals gallery available for hosting DCM solvent molecules within the network of molecules of **6f** (*bottom right*).

3. Conclusion

The disclosed strategy, upstream based on the use of LDA as the optimal base for the deprotonation of more or less nitrated N-aryl benzimidazole precursors dedicated to react with $ClPPh_2$, allowed a pioneering exploration of the coordination chemistry of nitro-aromatic phosphines as neutral electron-poor ligands with decreased σ-donating ability. The approach and results open natural prospects in organometallic chemistry such as the synthesis of tri- or tetra-nitro counterparts of the ligands **3**, the design of chelating diphosphine congeners, and the comparison with possible analogous complexes of nitrated triphenylphosphines such as $(4\text{-}NO_2\text{-}C_6H_4)_3P$ standing as a paradigm. As a preliminary analysis, reduction of the P atom of known *p*-nitrophenylphosphine oxides with the classical $HSiCl_3$ reagent is however expected to be tricky: in spite of an early report,[15e] recent results indeed indicate that competing reduction of the nitro group by $HSiCl_3$ could occur, even under milder conditions.[43] In an alternative strategy, (4-nitrophenyl)diphenylphosphine, partly described 40 years ago,[15b,20] was targeted from 4-nitro-iodobenzene and $ClPPh_2$ but could not be isolated, and further efforts in this direction are naturally envisaged. Nevertheless, targeting the particular category of the benzimidazolyllphosphine complexes **4** and **5** gave the opportunity of evidencing unique features such as: (i) empirical binary "orthogonal spectroscopic indicators" of the presence or not of nitro groups on distinct parts of the ligand (the benzimidazole core and the N-aryl substituent), based on an observed contrast between two ranges of values separated by *ca* 5 times the spectroscopic resolutions: 10 cm^{-1} and 30 ppm, respectively for the ν_{CO} and δ_{Rh} probes at the RhCl(CO) center; (ii) in the dicationic complex **5a'**, an electrostatic sandwiching of a chloro ligand by two imidazolium rings resulting from a packing effect, and possibly balanced by enhanced polarization of the Rh–Cl bond; (iii) serendipitous finding of an organic-organometallic clathrate of high solvent content (the DCM solvate complex **6f**). A more general occurrence of such features could be sought for in other systems involving other

transition metals (Ni, Pd, Pt...) and ligands or co-ligands thereof. Finally, beyond coordination chemistry, the results are naturally aimed at exploring the use such complexes in homogeneous catalysis.

4. Experimental section

4.1. General remarks

THF and diethyl ether were dried and distilled over sodium-benzophenone. Pentane and dichloromethane (DCM) were dried with a PureSolv-MD-5 Innovative Technology system for the purification of solvents. $[Rh(COD)Cl]_2$ and other reagents were employed as received from commercial sources, in particular, solutions of *n*-BuLi were 2.5 M in hexane. All reactions were carried out under an argon atmosphere by using Schlenk and vacuum line techniques. Column chromatography was carried out on silica gel (60 Å, C.C 70-200 μm). Previously reported procedures were used for the preparation of the phosphines and their precursors, in particular for the previously described compounds **1b** and **1c**,[44] **1d** and **1e**,[45] **2a**,[46] and **3a**.[47]

4.2. Procedures for the preparation of new compounds

For the characterization of the reported compounds by ^{1}H, ^{31}P ,^{13}C NMR and IR spectroscopy, by mass spectrometry, and by melting point, see SI

Preparation of 2b and **2c**.[45] A mixture of **1b** (2.69 g, 16.5 mmol), CuI (0.263 g, 1.38 mmol), 1,10-phenanthroline (0.48 g, 2.76 mmol), Cs_2CO_3 (9.42 g, 28.9 mmol) was evacuated twice and back-filled with argon in a dried Schlenk tube, then iodobenzene (1.52 ml, 13.8 mmol) and DMF (20 ml) was added with a syringe. The reaction mixture was stirred at 100°C for 48 h. After the mixture was cooled down to ambient temperature, the solution was filtered on silica gel, extracted with EtOAc, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluted with a 3/2

EtOAc/pentane mixture to deliver **2b** (2.108 g, 8.8 mmol, 64%) and **2c** (0.75g, 3.1 mmol, 23%) as yellow solids.

Preparation of 2f and **2g**.[48] A mixture of **1b** (1.63 g, 10 mmol) and NaOH (0.40g, 10 mmol) in 20 ml DMF was treated with 4-nitrofluorobenzene (2.12 ml, 20 mmol) at r. t. under argon. The mixture was stirred at 70°C for 5 h before addition of water. The resulting suspension was extracted with EtOAc (3× 40 mL), and the organic layer were combined, dried over $MgSO_4$ and concentrated to dryness under reduced pressure. Column chromatography of the residue on silica gel eluted with a 3/2 EtOAc/pentane mixture afforded the corresponding products **2f** (1.51 g, 5.3 mmol, 53 %) and **2g** (0.97 g, 3.4 mmol, 34 %) as yellow solids.

The same procedure from **1e** afforded **2e** as a yellow solid in 95 % yield. Starting from **1h**, and changing the chromatographic eluting system to a 1/1 EtOAc/pentane mixture, **2h** was obtained as a yellow solid in 86 % yield.

General procedure for preparation of the nitro-aromatic phosphines 3b-c, **3e-h**

A solution of **2a-c**, **2e-h** (1 equiv.) in THF was treated with a solution of freshly prepared LDA (1.2 equiv.) at -78°C. The mixture was slowly warmed up to -40°C, then stirred for 1 hat this temperature. After cooling back to -78°C, chlorodiphenylphosphine was added dropwise and the solution was slowly warmed up, then stirred at r.t. for 4 h. After addition of a saturated aqueous NH_4Cl solution and dilution with DCM, the aqueous layer was separated and the organic layer was dried over $MgSO_4$ and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel eluted with a 3/1 DCM/pentane mixture to give the corresponding products as yellow solids (for more details, see SI): **3a** (78 %), **3b** (83 %), **3c** (70 %), **3e** (62 %), **3f** (77 %), **3g** (45 %), **3h** (< 5 %).

General procedure for generation of the phosphine oxides 3xO (x = a-c, e-g)

The phosphine oxides were generated according to a previously reported procedure,[49] by treatment of a solution **3x** in THF with H_2O_2 (3 equiv.) at room temperature under TLC monitoring. After addition of $NaHCO_3$ and $Na_2S_2O_3$ solutions, the reaction mixture was separated, and the aqueous layer was extracted with DCM. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure affording the corresponding phosphine oxide in quantitative ^{31}P NMR spectroscopic yield without further purification. The products were analyzed by ^{31}P NMR spectroscopy only (see Table 2), except for **3aO** and **3bO** which were more completely characterized (see SI).

General procedures for preparation of rhodium complexes

Method A. A solution of **3x** (**x** = **b**, **f**, **e**) and $[Rh(cod)Cl]_2$ (0.5 equiv.) in DCM was stirred at r. t. for 4 h. After concentration under reduced pressure, the residue was washed with pentane and dried to afford the corresponding rhodium complex as brown solids: **4b** (95 %), **4e** (93 %), **4f** (94 %).

A solution of **4x** and the corresponding phosphine **3x** (1 equiv.) in DCM was treated with bubbling carbon monoxide for 15 min. After concentration under reduced pressure, the residue was washed with diethyl ether (or a DCM/pentane mixture) to give the corresponding rhodium complex **5b** (60 %), **5e** (74 %), **5f** (76 %). Minor amounts of the dimeric rhodium complex **6b** (18 %)**, 6e** (14 %) or **6f** (15 %) were also detected by ^{31}P NMR spectroscopy of the crude material (approximate spectroscopic yields given). Crystals of **6f** deposited from a DCM solution could be characterized by XRD analysis (see section 4.4 and SI).

Method B. A solution of **3x** (**x** = **a**, **c**, **g**) and $[Rh(cod)Cl]_2$ (0.25 equiv.) in DCM was stirred at r. t. for 4 h. Carbon monoxide was then bubbled through the solution for 15 min. After evaporation of the solvent under reduced pressure, the crude mixture was washed with diethyl ether (or a DCM/pentane mixture) to give the corresponding rhodium complex **5a** (79 %), **5c**

(81 %) or **5g** (73 %) as a yellow solid. Minor amounts of the dimeric rhodium complex **6c** (4 %) or **6g** (13 %) were also detected by ^{31}P NMR spectroscopy of the crude material (approximate spectroscopic yields given).

Rhodium complex 5a'. To a solution of **3a** (152 mg, 0.4 mmol) in DCM (4 mL) at –90°C was added methyl trifluoromethanesulfonate (45 µL, 0.4 mmol). The mixture was slowly warmed up to -40°C and stirred for 2 h. After evaporation of the solvent under reduced pressure, the residue was washed with cold pentane, dried under reduced pressure and then analyzed as a 5:1 N^+Me:P^+Me mixture of the methylation products of **3a**, which could not be separated. To a solution of this mixture in DCM (10 mL) was added $[Rh(cod)Cl]_2$ (41 mg, 0.083 mmol), and stirring was pursued at r. t. for 4 h. Carbon monoxide was then bubbled through the solution for 15 min. The solvent was evaporated under reduced pressure, and the residue was washed with diethyl ether to afford **5a'** (130 mg, 68 %) as a yellow solid.

4.3. ^{103}Rh NMR spectroscopy

^{103}Rh/^{31}P{^{1}H} HMQC spectra were recorded on a Bruker AV400 spectrometer, equipped with a three-canal probe H{P}{X}- TBI 5 mm using saturated solutions of **5x** in CD_2Cl_2 (in the cases of **5e** and **5f**, saturated concentration did not allow achieving sufficient acquisition in available time). A preliminary search for the ^{103}Rh resonances was performed through ^{31}P{^{1}H} experiments with ^{103}Rh inversion using a sequence adapted from the literature giving a narrow range for ^{103}Rh chemical shifts.[50] In this range, precise chemical shifts of ^{103}Rh were measured via an inverse correlation HMQC using both ^{103}Rh-^{31}P coupling constants. The exact spectrometer ^{1}H frequency of $\nu_0 =$ 400.1318 MHz corresponds to the resonance of. tetramethylsilane. The ^{103}Rh frequency ratio Ξ can be assigned to either the formal value Ξ = 3.16 % (for which rhodium metal is just an approximate reference giving $\delta_{^{103}Rh} \approx 0$ ppm),[51] or to the observable value Ξ' = 3.186447 % defined from the real reference $Rh(acac)_3$ (for

which $\delta_{^{103}Rh}$ = 0 ppm if saturated in $CDCl_3$ solution).[52] Each frequency ratio defines its own chemical shift scale in ppm: $\delta = (\nu - \Xi\ \nu_0)/(\Xi\ \nu_0)\ 10^6$ and $\delta' = (\nu - \Xi'\ \nu_0)/(\Xi'\ \nu_0)\ 10^6$, where ν is the physical resonance frequency observed for the nominal field of the spectrometer. By elimination of ν, the scales are related by the equation: $\delta = \delta'\ \xi + (\xi - 1)\ 10^6$, where $\xi = \Xi'/\Xi$ = 1.008369 (giving $\delta(Rh(acac)_3)$ = 8369 ≈ 8358 ppm for $\delta'(Rh(acac)_3)$ = 0). [51a] The $\delta_{^{103}Rh}$ values in Table 2 are given in both scales.

4.4. Crystallographic studies

Intensity X-ray diffraction data from single crystals were collected at low temperature on an Apex2 Bruker diffractometer equipped with a 30W air-cooled microfocus source (λ = 0.71073 Å) or on an Oxford-Diffraction Gemini (λ = 0.71073 or 1.54180 Å). The structures were solved using direct methods or SUPERFLIP, and refined by means of least-squares procedures on *F* using the programs of the PC version of CRYSTALS. Atomic scattering factors were taken from the International Tables for X-Ray Crystallography.[53] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using a riding model. Absorption corrections were introduced using the program MULTISCAN. For the free phosphines **3b** and **3f**, it was not possible to resolve diffuse electron-density residuals (enclosed solvent molecules). Treatment with the SQUEEZE facility from PLATON resulted in a smooth refinement.[54]

Supporting information. Supporting information for this article is available on the WWW under http://dx.doi.org/… It includes yields, spectroscopic and other characterizations of all new compounds. ^{1}H, ^{31}P, ^{13}C,^{103}Rh-$^{31}P\{^{1}H\}$ HMQC NMR spectra and crystallographic data are also provided.

Acknowledgements. C. Z. thanks the China Scholarship Council for financial support. R. C. thanks the CNRS for half a teaching sabbatical in 2014-2015 and 2015-2016. A determining support was also indirectly provided by the ANR program (ANR-11-BS07-016-01). The authors are also indebted to Dr. Valérie Maraval for efficient logistic management.

References and notes

[1] C. Lepetit, V. Maraval, Y. Canac, R. Chauvin, *Coord. Chem. Rev*. **2016**, *308 II,* 59-75.

[2] a) Nelson, D. J.; Nolan, S. P. *Chem. Soc. Rev*. **2013**, *42*, 6723-6753. b) Melaimi, M.; Soleilhavoup, M.; G. Bertrand, G. *Angew. Chem. Int. Ed*. **2010**, *49*, 8810-8849. c) *Top. Organomet. Chem.* 'Late transition metal complexes of neutral η^1-carbon ligands: R. Chauvin, Y. Canac, Eds, Springer, **2010**, *30*, 1-252. d) J. Vignolle, X. Cattoën, D. Bourissou, *Chem. Rev*. **2009**, *109*, 3333-3384. e) S. Díez-González, N. Marion, S. P. Nolan, *Chem. Rev*. **2009**, *109*, 3612-3676. f) F. E. Hahn, M. C. Jahnke, *Angew. Chem. Int. Ed*. **2008**, *47*, 3122-3172. g) Y. Canac, M. Soleihavoup, S. Conejero, G. Bertrand, *J. Organomet. Chem*. **2004**, *689*, 3857-3865.

[3] C. Maaliki, C. Lepetit, Y. Canac, C. Bijani, C. Duhayon, R. Chauvin, *Chem. Eur. J.* **2012**, *18*, 7705-7714.

[4] See for example: a) R. L. Pruett, J. A. Smith, *J. Org. Chem.* **1969**, *34*, 327-330; b) K. Nozaki, T. Nanno, H. Takaya, *J. Organomet. Chem*. **1997**, *527*, 103-108; c) R. A. Baber, M. L. Clarke, K. M. Heslop, A. C. Marr, A. G. Orpen, P. G. Pringle, A. Ward, D. E. Zambrano-Williams, *Dalton Trans*. **2005**, 1079-1085; d) F. Doro, J. N. H. Reek, P. W. N. M. van Leeuwen, *Organometallics* **2010**, *29*, 4440-4447; e) Q. Liu, L. Wu, I. Fleischer, D. Selent, R. Franke, R. Jackstell, M. Beller, *Chem. Eur. J*. **2014**, *20*, 6888-6894.

[5] See for example: a) M. F. Ernst, D. M. Roddick, *Inorg. Chem.* **1989**, *28*, 1624-1627; b) M. Brookhart, W. A. Chandler, A. C. Pfister, C. C. Santini, P. S. White, *Organometallics* **1992**, *11*, 1263-1274; c) D. C. Smith Jr., E. D. Stevens, S. P. Nolan, *Inorg. Chem.* **1999**, *38*, 5277-5281; d) D. R. Palo, C. Erkey, *Organometallics* **2000**, *19*, 81-86; e) F. Berhal, O. Esseiva, C. H. Martin, H. Tone, J.-P. Genet, T. Ayad, V. Ratovelomanana-Vidal, *Org. Lett*. **2011**, *13*, 2806-2809; f) B. G. Anderson, J. L. Spencer, *Chem. Eur. J*. **2014**, *20*, 6421-6432.

[6] a) I. V. Komarov, M. Y. Kornilov, A. A. Tolmachev, A. A. Yurchenko, E. B. Rusanov and A. N. Chernega, *Tetrahedron* **1995**, *51*, 11271-11280; b) M. Enders, O. Fritz, H. Pritzkow, *Z. Anorg. Allg. Chem*. **2004**, *630*, 1501-1506; c) P. Antognazza, T. Benincori, S. Mazzoli, F. Sannicolo, T. Pilati, *Phosphorus Sulfur Silicon* **1999**, *144-146*, 405-408. d) T. Benincori, E. Brenna, F. Sannicolo, L. Trimarco, P. Antognazza, E. Cesarotti, F. Demartin, T. Pilati, G. Zotti, *J. Organomet. Chem*. **1997**, *529*, 445-453; e) N. Debono, Y. Canac, C. Duhayon, R. Chauvin, *Eur. J. Inorg. Chem*. **2008**, 2991-2999; f) I. Abdellah, N. Debono, Y. Canac, L. Vendier, R. Chauvin, *Chem. Asian. J.* **2010**, *5*, 1225-1231.

[7] For pioneering works, see: a) U. Zoller, *Tetrahedron* **1988**, *44*, 7413-7426; b) N. Kuhn, J. Fahl, D. Blaeser, R. Boese, *Z. Anorg. Allg. Chem*. **1999**, *625*, 729-734; c) N. Kuhn, M. Goehner, G. Henkel, *Z. Anorg. Allg. Chem*. **1999**, *625*, 1415-1416; d) J. Sirieix, M. Obberger, B. Betzemeier, P. Knochel, *Synlett* **2000**, *11*, 1613-1615; e) M. Azouri, J. Andrieu, M. Picquet, P. Richard, B. Hanquet, I. Tkatchenko, *Eur. J. Inorg. Chem*. **2007**, 4877-4883.

[8] For reviews, see: (a) Y. Canac, C. Maaliki, I. Abdellah, R. Chauvin, *New. J. Chem*. **2012**, *36*, 17-27; b) S. Gaillard, J. L. Renaud, *Dalton Trans*. **2013**, 7255-7270; c) M. Alcarazo, *Chem. Eur. J.* **2014**, *20,* 7868-7877; d) M. Alcarazo, *Acc. Chem. Res.* **2016**, *49*, 1797-1805.

[9] I. Abdellah, C. Lepetit, Y. Canac, C. Duhayon, R. Chauvin, *Chem. Eur. J*. **2010**, *16*, 13095-13108.

[10] a) C. Mboyi, C. Maaliki, A. Mankou Makaya, Y. Canac, C. Duhayon, R. Chauvin, *Inorg. Chem*. **2016**, *55*, 11018-11027; b) G. Mehler, P. Linowski, J. Carreras, A. Zanardi, J. W. Dube, M. Alcarazo, *Chem. Eur. J*. **2016**, *22*, 15320-15327.

[11] J. Petuskova, H. Bruns and M. Alcarazo, *Angew. Chem., Int. Ed*. **2011**, *50*, 3799-3802.

[12] a) B. Vabre, Y. Canac, C. Duhayon, R. Chauvin, D. Zargarian, *Chem. Commun*. **2012**, *48*, 10446-10448; b) I. Abdellah, Y. Canac, C. D. Mboyi, C. Duhayon, R. Chauvin, *J. Organomet. Chem*. **2015**, *776*, 149-162; c) B. Vabre, Y. Canac, C. Lepetit, C. Duhayon, R. Chauvin, D. Zargarian, *Chem. Eur. J*. **2015**, *21*, 17403-17414.

[13] C. Hansch, A. Leo, R. W. Taft, *Chem. Rev*. **1991**, *91*, 165-195.

[14] Generalization of the Hammett equation, originally defined for X/H-substitution (–H → –X), to aza-analogation (=CH– → =N–) and protoaza-analogation (=CH– → =NH^+–) gives the following values for the corresponding constants: $\sigma_{m(N)} = 0.45$, $\sigma_{p(N)} = 0.76$, $\sigma_{m(NH+)} = 2.09$ and $\sigma_{p(NH+)} = 2.34$. Comparison with the NO_2/H-substitution values ($\sigma_m = 0.71$, $\sigma_p = 0.78$) indicates that neutral azalogation has a significant, albeit weaker, electron-withdrawing effect, but suggests that N-protonation (representative of N-alkylation) has a twice stronger effect ($\sigma_{m(NH+)} - \sigma_{m(N)} = 1.64$, $\sigma_{p(NH+)} - \sigma_{p(N)} = 1.58$). See: C. D. Jonhson, *The Hammet Equation*, pp. 99-101, Cambridge University Press, London, 1973.

[15] a) A. Stachlewska-Wroblowa, K. Okon, *Bull. Acad. Pol. Sci, Ser. Sci. Chim.* **1961**, *9*, 297-301; b) G. P. Schiemenz, *Chem.Ber*. **1966**, *99*, 514-519; c) G. P. Schiemenz, K. Roehlk, *Chem.Ber*. **1971**, *104*, 1219-1233; d) J. I. G. Cadogan, D. J. Sears, D. M. Smith, *J. Chem. Soc. C* **1969**, 1314-1318; e) G. P. Schiemenz, P. Nielsen, *Phosphorus Sulfur* **1985**, *21*, 259-266.

[16] DFT calculations at the B3PW91/6-31G(d,p) level, without solvent correction (vacuum), using the Firefly software (see SI): a) A. A. Granovsky, *Firefly version 8,*

http://classic.chem.msu.su:gran:firefly:index.html) which is partially based on the GAMESS (US) source code; b) M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, J. A. Montgomery, *J. Comput. Chem*. **1993**, *14*, 1347-1363.

[17] G. A. Olah, B. G. B. Gupta, S. C. Narang, *J. Am. Chem. Soc.* **1979**, 5317-5322.

[18] a) M. Mąkosza, M. Paszewski, D. Sulikowski, *Synlett* **2008**, 2938-2940; b) J. Xu, P. B. Zhang, Y. Z. Gao, Y. Y. Chen, G. Tang, Y. F. Zhao, *J. Org. Chem*. **2013**, *78*, 8176-8183. c) M. Hayashi, T. Matsuura, I. Tanaka, H. Ohta, Y. Watanabe, *Org. Lett.* **2013**, *15*, 628-631; d) H. Zhang, X. Y. Zhang, D. Q. Dong, Z. L. Wang, *RSC. Adv.* **2015**, *5*, 52824-52831; e) D. V. Aleksanyan, Z. S. Klemenkova, A. A. Vasil'ev, A. Y. Gorenberg, Y. V. Nelyubina, V. A. Kozlov, *Dalton Trans*. **2015**, *44*, 3216-3226.

[19] Model nitroaryl-phosphine ligands in Rh(II), Ru(II) or Fe(II) complexes have however been calculated at the DFT level of theory: (a) P. Hirva, P. Lahuerta, J. Perez-Prieto, *Theor. Chem. Acc*. **2005**, *113*, 63-68; b) P. Hirva, E. Julio, J. Lloret, P. Lahuerta, J. Perez-Prieto, *Inorg. Chem.* **2007**, *46*, 2619-2626; d) E. Pump, L. Cavallo, C. Slugovc, *Monatsch. Chem*. **2015**, *146*, 1131-1141; d) B. Mondal, F. Neese, S. Ye, *Inorg. Chem.* **2016**, *77*, 5438-5444.

[20] G. P. Schiemenz, M. Finzenhagen, *Liebigs Ann. Chem*. **1976**, 2126-2135;

[21] a) N. F. Blank, J. R. Moncarz, T. J. Brunker, C. Scriban, B. J. Anderson, O. Amir, D. S. Glueck, L. N. Zakharov, J. A. Golen, C. D. Incarvito, A. L. Rheingold, *J. Am. Chem. Soc.* **2007**, *129*, 6847-6858. b) N. Nowrouzi, S. Keshtgar, E. B. Jahromi, *Tetrahedron Lett.* **2016**, *57*, 348-350.

[22] a) F. Y. Kwong, C. W. Lai, Y. Tian, K. S. Chan, *Tetrahedron Lett.* **2000**, *41*, 10285-10289; b) S. E. Martin, M. Bonaterra, R. A. Rossi, *J. Organomet. Chem.* **2002**, *664*, 223-227.

[23] For recent examples in the aryl-heteroaryl series, see: a) N. V. Artemova, M. N. Chevykalova, Y. N. Luzikov, I. E. Nifant'ev, E. E. Nifant'ev, *Tetrahedron* **2004**, *60*, 10365-10370; b) D. M. Zink, D. Volz, T. Baumann, M. Mydlak, H. Flügge, J. Friedrichs, M. Nieger, S. Bräse, *Chem. Mater*. **2013**, *25*, 4471-4486.

[24] a) G. Bartoli, *J. Chem. Soc. Perkin Trans. II* **1989**, *2*, 573-578. b) G. Bartoli, M. Bosco, R. Dalpozzo, L. Grossi, *Nato Science Series C: Mathematical and Physical Sciences* **1989**, *257*, 489-502.

[25] G. Piersanti, L. Giorgi, F. Bartoccini, G. Tarzia, P. Minetti, G. Gallo, F. Giorgi, M. Castorina, O. Ghirardi, P. Carminati, *Org. Biomol. Chem*. **2007**, *5*, 2567-2571.

[26] C. A. Tolman, *Chem. Rev*. **1977**, *77*, 313-348.

[27] a) Y. Canac, N. Debono, L. Vendier, R. Chauvin, *Inorg. Chem*. **2009**, *48*, 5562-5568; b) C. Barthes, C. Lepetit, Y. Canac, C. Duhayon, D. Zargarian, R. Chauvin, *Inorg. Chem*. **2013**, *52*, 48-58.

[28] C. J. Elsevier, B. Kowall, H. Kragten, *Inorg. Chem*. **1995**, *34*, 4836-4839.

[29] a) A. Klapars, J. C. Antilla, X. Huang, S. L. Buchwald. *J. Am. Chem. Soc.* **2001**, *123*, 7727-7729. b) S. Harkal, F. Rataboul, A. Zapf, C. Fuhrmann, T. Riermeier, A. Monsees, M. Beller, *Adv. Synth. Catal.* **2004**, *346*, 1742-1748.

[30] L. Zhu, L. Cheng, Y. Zhang, R. Xie, J. You, *J. Org. Chem.* **2007**, *72*, 2737-2743.

[31] The regio-isomers are markedly distinguished by the amidine C*H* ^{1}H NMR chemical shift, at 8.70 ppm for **2b** and 8.39 ppm for **2c**, *vs* 8.35 ppm for **2a**: assuming that the substituent effect (*vs* H in **2a**) is first determined by the shortest bond path to the NO_2 group, the C5 path of **2b** appears more efficient than the C3NC path of **2c**.

[32] The dinitro compounds **2f** and **2g** could be separated by column chromatography, but their lack of solubility in organic solvent happened to be detrimental to their isolation in highly

pure form. Noteworthy, the Buchwald's procedure from **1b-c** and 4-iodonitrobenzene was found much less efficient, giving **2f** and **2g** in 25 % and 12 % yield, respectively.

[33] At a higher temperature of –40°C, LDA was indeed reported to reduce nitroarenes to aminoarenes and oxyazoarenes *via* single electron transfer (SET): A. L. Wang, E. Biehl, *ARKIVOC* **2002**, 71-75

[34] L. H. Zou, Z. B. Dong, C. Bolm, *Synlett* **2012**, *23*, 1613-1616.

[35] CCDC no 1496156 (**3b**), 1496157 (**3c**), 1496158 (**3f**), 1496159 (**3e**), 1496162 (**5a**), 1496160 (**5b**), 1496161 (**5c**), 1496163 (**5f**), 1496164 (**5g**), 1496165 (**5a'**) and 1496166 (**6f**) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/getstructures

[36] N-alkyl congeners of N-phenyl imidazolo-monophosphines (non-benzannelated analogues of **3a**) were reported to undergo selective N-methylation with Me_2SO_4 or $[Me_3O][BF_4]$, and selective P-methylation with MeI: A. A. Tolmachev, A. A. Yurchenko, A. S. Merculov, M. G. Semenova, E. V. Zarudnitskii, V. V. Ivanov, A. M. Pinchuk, *Heteroat. Chem*. **1999**, *10*, 585-597.

[37] a) Even in the neutral ligand sub-series, the C-O distance takes the smallest value of 1.11 Å in **5a** for the *a priori* most electron-donating representative **3a** and significantly greater values of *ca* 1.16 Å in **5c** and **5f-g** for the corresponding nitro-ligands **3c** and **3f-g** (Table 1); b) F. R. Hartley, *Chem. Soc. Rev*. **1973**, 163-179.

[38] C. J. Elsevier, B. Kowall, H. Kragten, *Inorg. Chem*. **1995**, *34*, 4836-4939.

[39] See for example: a) T. Vorfalt, S. Leuthußer, H. Plenio, *Angew. Chem. Int. Ed*. **2009**, *48*, 5191-5194; b) T. Sato, Y. Hirose, D. Yoshioka, S. Oi, *Organometallics* **2012**, *31*, 6995-7003; c) Z.-Q. Zhu, M.-Y. Jiang, J.-H. Lin, C.-P. Zhang, X.-C. Hang, C.-G. Zheng, Q.-Y. Chen, J.-

C. Xiao, *Synlett* **2009**, 2305-2308; d) T. Ritter, M. W. Day, R. H. Grubbs, *J. Am. Chem. Soc*. **2006**, *128*, 11768-11769; e) M. G. Hobbs, C. J. Knapp, P. T. Welsh, J. Borau-Garcia,T. Ziegler, R. Roesler, *Chem. Eur. J*. **2010**, *16*, 14520-14533 and references therein; f) D. A. J. Harding, E. G. Hope, K. Singh, G. A. Solan, *Organometallics* **2012**, *31*, 1518-1523 and references therein.

[40] a) R. J. Haines, N. D. C. T. Steen, *J. Chem. Soc. Chem. Comm.* **1981**, 407-408; b) R. J. Haines, N. D. C. T. Steen, *J. Chem. Soc. Dalton Trans.* **1983**, 2229-2234; c) N. C. Yang, H. Shou, T. Wang, J. Masnovi, *J. Am. Chem. Soc.* **1980**, *102*, 6654-6656; d) J. P. Farr, M. M. Olmstead, C. H. Hunt, A. L. Balch, *Inorg. Chem.* **1981**, *20*, 1182-1187; e) H. Braunschweig, M. Forster, K. Radacki, *Angew. Chem. Int. Ed.* **2006**, *45*, 2132-2134; f) F. A. Cotton, C. T. Eagle, A. C. Price, *Inorg. Chem.* **1988**, *27*, 4362-4368; g) R. Y. Haines, M. Laing, E. Meintjies, F. Sommerville, *J. Organomet. Chem.* **1981**, *215*, C17-C19; h F. E. Wood, M. M. Olmstead, A. L. Balch, *J. Am. Chem. Soc.* **1983**, *105*, 6334-6335; i) R. E. Marsh, M. M. Olmstead, W. P. Schaefer, V. Schomakert, *Inorg. Chem.* **1993**, *32*, 4658-4659; j) L. A. Oro, M. A. Ciriano, B. E. Villarroya, A. Tiripicchio, F. J. Lahoz, *J. Chem. Soc. Chem. Comm.* **1984**, 521-522; k) B. R. Sutherland, M. Cowie, *Inorg. Chem.* **1984**, *23*, 1290-1297; l) A. L. Balch, L. A. Fossett, R. R. Guimerans, M. M. Olmstead, *Organometallics* **1985**, *4*, 781-788; m) L. Gelmini, D. W. Stephan, *Inorg. Chim. Acta*, **1985**, *98*, L3-L6; n) R. H. Dawson, M. M. Harding, S. Maginn, A. K. Smith, *Inorganica Chimica Acta*, **1988**, *149*, 281-284; o) S. Jaaskelainen, M. Haukka, H. Riihimaki, J. T. Pursiainen, T. A. Pakkanen, *J. Organomet. Chem.* **2004**, *689*, 1064-1070; p) B. T. Heaton, C. Jacob, J. T. Sampanthar, *J. Chem. Soc., Dalton Trans.* **1998**, 1403-1410; q) L. A. Oro, M. A. Ciriano, B. E. Villarroya, A. Tiripicchio, F. J. Lahoz, *J. Chem. Soc., Dalton Trans*. **1985**, 1891-1898; r) H. Song, R. C. Haltiwanger, M. R. DuBois, *Organometallics* **1987**, *6*, 2022-2028.

[41] a) For a recent general review, see: G. Cavallo, P. Metrangolo, R. Milani, T. Pilati, A. Priimagi, G. Resnati, G. Terraneo, *Chem. Rev*. **2016**, *116*, 2478-2601; b) *Halogen Bonding in Crystal engineering, fundamentals and applications*, *Cryst. Growth Des.* virtual issue, **2012**, Volume *vi* (8), http://pubs.acs.org/page/cgdefu/vi/8; c) F. M. Amombo Noa, S. A. Bourne, L. R. Nassimbeni, *Cryst. Growth Des.* **2015**, *15*, 3271-3279.

[42] a) S. Kitagawa, K. Uemura, *Chem. Soc. Rev*. **2005**, *34*, 109-119; b) F. Bottino, P. Finocchiaro, J. Lipkowski, A. Mamo, S. Pappalardo, K. Suwinska, *J. Inclusion Phenom. Mol. Recognit. Chem*. **1991**, *11*, 41-48; c) A. R. Albunia, R. Graf, *Soft Materials* **2011**, *9*, 183-198; d) B. T. Ibragimov, *CrystEngComm* **2007**, *9*, 111-118; e) V. G. Saraswatula, M. A. Bhat, S. Bhattacharya, B. K. Saha, *J. Chem. Sci*. **2014**, *126*, 1265-1273; f) see for example: D. V. Soldatov, *J. Chem. Cryst*. **2006**, *36*, 747-768; g) T. Kitasawa, S. Nishikiori, R. Kuroda, T. Iwamoto, *Chem. Lett*. **1988**, 1729-1732; h) see for example: K. Vellingri, A. Deep, K.-H. Kim, *ACS Appl. Mater. Interfaces* **2016**, *8*, 29835-29857; i) M. L. Kilkenny, L. R. Nassimbeni, *J. Chem. Soc., Dalton Trans*. **2001**, 3065-3068; j) T. Jacobs, L. J. Barbour, *CrystEngComm* **2013**, *15*, 1512-15414; k) Z. Dai, A. J. Metta-Magana, J. E. Nunez, *Inorg. Chem*. **2014**, *53*, 7188-7196.

[43] a) M. Orlandi, F. Tosi, M. Bonsignore, M. Benaglia, *Org. Lett*. **2015**, *17*, 3941-3943; b) M. Orlandi, M. Benaglia, F. Tosi, R. Annunziata, F. Cozzi, *J. Org. Chem*. **2016**, *81*, 3037-3041.

[44] Z. H. Zhang, L. Yin, Y. M. Wang, *Catal. Commun.* **2007**, *8*, 1126-1131.

[45] a) G. A. Zhumabaeva, S. K. Kotovskaya, N. M. Perova, V. N. Charushin, O. N. Chupakhin, *Russ.Chem.Bull.Int.Ed*., **2006**, *55*(7), 1243-1247; b) K. Kincaid, J. Beckman, A. Zivkovic, R. L. Halcomb, J. W. Engels, R. D. Kuchta, *Nucleic Acids Research* **2005**, *33*, 2620-2628.

[46] L. B. Zhu, P. Guo, G. C. Li, J. B. Lan, R. G. Xie, J. S. You, *J. Org. Chem.* **2007**, *72*, 8535-8538.

10.1002/asia.201701078

[47] a) S. Harkal, F. Rataboul, A. Zapf, C. Fuhrmann, T. Riermeier, A. Monsees, M. Beller, *Adv. Synth. Catal.* **2004**, *346*, 1742-1748; b) N. Debono, Y. Canac, C. Duhayon, R. Chauvin, *Eur. J. Inorg. Chem.* **2008**, 2991-2999.

[48] C. B. Liu, H. Wang, X. Xing, Y. Xu, J. A. Ma, B. Zhang, *Tetrahedron Lett.* **2013**, *54*, 4649-4652.

[49] Y. Unoh, T. Satoh, K. Hirano, M. Miura, *ACS Catal.* **2015**, *5*, 6634-6639.

[50] A. Bax, *J. Magn. Reson*. **1983**, *52*, 76-80.

[51] a) B. E. Mann in *NMR of Newly Accessible Nuclei*, *Vol. 2*, P. Laszlo Ed., Chapt. 11, pp. 301-318, Academic Press, New York, 1983; b) J. M. Ernsting, S. Gaemers, Cornelis J. Elsevier, *Magn. Reson. Chem*. **2004**, *42*, 721-736.

[52] a) R. Benn, A. Rufinska, *Angew. Chem. Int. Ed. Engl*. 1986, 25, 861-881; b) R. K. Harris, E. D. Becker, S. M. Cabral de Mennezes, R. Goodfellow, P. Granger, *Pure Appl. Chem*. **2001**, *73*, 1795-1818; c) R. K. Harris, E. D. Becker, S. M. Cabral de Mennezes, P. Granger, R. E. Hoffman, K. H. Zilm, *Pure Appl. Chem*. **2008**, *80*, 59-84.

[53] J. A. Ibers, W. C. Hamilton, *International Tables for X-Ray Crystallography*, vol. IV, Kynoch Press, Birmingham, England, 1974.

[54] P. v. d. Sluis, A. L. Spek, *Acta Cryst. A* **1990**, *A46*, 194-201.

GRAPHICAL ABSTRACT