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Journal Name

ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

C–H Nickellation of Phenol-Derived Phosphinites: Regioselectivity and Structures of Cyclonickellated Complexes

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Abstract. This report describes the results of a study on the ortho-C-H nickellation of the aryl phosphinites i-Pr₂P(OAr) derived from the following four groups of substituted phenols: 3-R-C₆H₄OH (R= F (b), Me (c), MeO (d), Cl (e)); 3,5-R₂-C₆H₃OH (R= F (f), Me (g), Cl (h), OMe (i)); 2-R-C₆H₄OH (R= Me (j), Ph(k)); and 2,6-R₂-C₆H₃OH (R= Me (l), Ph (m)). No nickellation was observed with the phosphinites derived from the 3,5-disubstituted phenols g and h, and the 2,6disubstituted phenols I and m; in all other cases nickellation occurred at an ortho-C-H to generate either the Br-bridged dimers $[\{\kappa^{P}, \kappa^{C}-(i-Pr)_{2}POAr\}Ni(\mu-Br)]_{2}$ (**1b-1f**, **1j**, and **1k**) or the monomeric acetonitrile adduct $\{\kappa^{P}, \kappa^{C}-ArOP(i-Pr)_{2}POAr\}Ni(\mu-Br)]_{2}$ Pr)₂}Ni(Br)(NCMe) (1i-NCMe). Analysis of C-H nickellation regioselectivity with 3-R-C₆H₄OH pointed to the importance of substituent sterics, not electronics; nickellation occurred at the least hindered position either exclusively (for R = Me(c)). MeO(d), and Cl (e)) or predominantly (for R= F (b); 6:1). This conclusion is also consistent with the observation that C-H nickellation is possible with the 3,5-disubstituted aryl phosphinites bearing F and OMe, but not with the more bulky substituents Me or Cl. For the 2-substituted aryl phosphinites, C-H nickellation occurs at the unsubstituted ortho-C-H and not on the R substituent, regardless of whether the alternative C-H moiety of the substituent is sp^3 (R= Me (j)) or sp^2 (R= Ph (k)). The system thus reveals a strong preference for formation of 5-membered metallacycles. Consistent with this reactivity, no nickellation occurs with (2,6-R₂-C₆H₃O)P(*i*-Pr)₂. Tests with the parent dimer derived from *i*-Pr₂P(OPh) showed that conversion to the monomeric acetonitrile adduct is highly favored, going to completion with only a small excess of MeCN. All new cyclonickellated complexes reported in this study were fully characterized, including by single crystal X-ray diffraction studies. The solid state structures of the dimers **1b** and **1d** showed an unexpected feature; two halves of the dimers displayed non-coplanar conformations that place the two Ni(II) centers at shortened distances from each other (2.94-3.16 Å). Geometry optimization studies using DFT have shown that such non-coplanar conformations stabilize the complex, implying that the "bending" observed in these complexes is not caused by packing forces. Indeed, it appears that the occurrence of coplanar conformations in the solid state structures of these dimers is a simple consequence of packing forces rather than an intrinsic property of the compound.

Introduction

Chelation-assisted C-H metallation and derivatization is an attractive methodology for the sustainable synthesis of complex organic molecules.¹ This approach is generally considered to be even more powerful when (i) simple salts or derivatives of the more abundant 3d metals can serve as required metallic precursors, and (ii) the directing functional group(s) required for chelation can be installed and removed easily ("traceless functionalization").² From a practical point of view, another desired feature of metallation-functionalization protocols is that they proceed in a one-pot

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manner, thus bypassing the isolation and manipulation of the cyclometallated species that are thought to be intermediates in these processes. On the other hand, intercepting such key intermediates of the catalytic cycle and probing their properties can be potentially advantageous for rational design of new metallation-functionalization processes and their optimization. For instance, isolation of the cyclometallated species arising from the C-H metallation can facilitate the modelling of this step and allow a systematic study of the functionalization step as well.

The emergence over the past decade of an increasing number of reports on nickel-catalyzed C-H functionalization reactions has demonstrated that in this context Ni precursors can be viable alternatives to their more widely-used Pd counterparts.³ These developments and our longstanding interest in organonickel chemistry,⁴ including the synthesis and reactivities of pincer-type nickel complexes,⁵ led us to prepare nickellacyclic complexes via C-H nickellation and study their structures, stabilities, and functionalization aptitudes. The preparation of the orthonickellated phosphinite complexes [$\{\kappa^{P}, \kappa^{C}-(i-Pr)_{2}POAr\}Ni(\mu-Br)$]₂ or *trans-*{ κ^{P}, κ^{C} -

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⁺Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x



Scheme 1. Alternative protocols for preparation of orthonickellated complexes from aryl phosphinites.

 $ArOP(i-Pr)_2NiBr\{i-Pr_2P(OAr)\}$ derived from substituted phenols, $R-C_6H_4OH$, was reported recently (Scheme 1).^{6,7}

This first report outlined the impact of substituent R on relative cyclonickellation rates for $R-C_6H_4OP(i-Pr)_2$ (COOMe < Me < OMe), indicating that the C-H nickellation step follows an electrophilic mechanism; this finding was consistent with our postulates on how POCOP-type pincer ligands undergo C-H nickellation.⁸ This report also showed that the cyclonickellated complexes in question can be benzylated at the nickellated carbon, thus providing a proof of concept for the functionalization step.⁶ On the other hand, our initial results did not provide much insight on the regioselectivity of cyclonickellation, nor did they result in a broad scope for the functionalization step. It was thus evident that much was left to do to develop a better understanding of the factors that govern C-H nickellation and the reactivities of the resulting species.

As a continuation of our initial studies, we have examined the regioselectivity of C-H nickellation with aryl phosphinites R_nC₆H₍₅₋ _{n)}OP(*i*-Pr)₂ derived from substituted phenols. The results presented herein show that C-H nickellation of substrates derived from 3-R- C_6H_4OH (R = Me, OMe, Cl) takes place selectively at the less hindered ortho position, whereas nickellation of substrates derived from 2-R-C₆H₄OH (R = Me, Ph) takes place at the unsubstituted ortho C-H of the phenol ring, and not on the ring substituents. In contrast to the reactivity of these mono-substituted substrates, no nickellation takes place with disubstituted phosphinites derived from $2,6-R_2-C_6H_3OH$ (R = Me, Ph) or $3,5-R_2-C_6H_3OH$ (R = Me, Cl), whereas the less bulky analogues of the latter phosphinites (R = F, OMe) did undergo nickellation. The observed nickellation reactions led to the dimeric species $[\{\kappa^{P}, \kappa^{C} - (i-Pr)_{2}POAr\}Ni(\mu-Br)]_{2}$ in every case except with $3,5-(MeO)_2-C_6H_3OP(i-Pr)_2$, which produced the monomeric acetonitrile adduct $trans - {\kappa^{P}, \kappa^{C} - 3, 5 - (MeO)_{2} - C_{6}H_{3}OP(i-$ Pr)₂}NiBr(NCMe). The present report discusses these results in terms of the steric and electronic properties of the R-substituents, and describes the solid state structures and NMR spectra of the various cyclonickellated complexes obtained.

Results & Discussion

Revised procedure for cyclonickellation of arylphosphinites. Vabre et al.⁶ have reported that extended heating of the Ni(II) precursor {(*i*-PrCN)NiBr₂}_n in toluene with *i*-Pr₂P(OPh), **a**, and NEt₃ facilitates direct *ortho*-C-H nickellation; this reaction generated both the Br-bridged dinickel complex { $\kappa^{P}, \kappa^{C}-C_{6}H_{4}OP(i-Pr)_{2}$ }NiBr}₂ (**1a**) and its monomeric *i*-Pr₂P(OPh) adduct bearing a non-cyclometallated phosphinite, *trans*-{ $\kappa^{P}, \kappa^{C}-C_{6}H_{4}OP(i-Pr)_{2}$ }Ni{*i*-Pr₂P(OPh)}Br (**1a**-**P(OPh)(***i***-Pr)₂) (Scheme 1). Controlling the precise phosphinite: Niprecursor ratio in this protocol allowed the exclusive or predominant formation of one or the other of the two products. For example, using a 1.0 : 0.6 ratio gave the thermodynamically more favored mononickel adduct exclusively, whereas a 1 : 2 ratio gave the dinickel species.6**

To improve the atom-efficiency of the orthonickellation reaction under discussion, we probed the influence of various solvents with a view to favoring the formation of the dimeric species **1a**. Our tests showed that using acetonitrile as solvent led to orthonickellation at lower temperatures and over a shorter reaction time. This modified protocol also required only a small excess of the Ni(II) precursor to smoothly generate the monomeric MeCN adduct as a stable intermediate species, from which we could obtain the target Brbridged dimer after work-up (Scheme 1). In contrast, conducting the nickellation reactions in THF or ethyl acetate showed rates that were intermediate between those observed in toluene and acetonitrile, such that the nickellation was incomplete after 24 h.

We believe that the main advantages of using acetonitrile in this C-H nickellation protocol, i.e., exclusive access to the dimeric species over shorter reaction times, can be attributed to two factors. First, acetonitrile reaction mixtures remain homogeneous throughout the entire reaction span, thus providing a greater effective concentration of Ni and maintaining a Ni : phosphinite ratio of ≈ 1 : 1. Second, formation of the undesired adduct **1a-P(OPh)(***i***-Pr)**₂ during the reaction is circumvented by the facile formation of the analogous acetonitrile adduct, as illustrated in Scheme 1. This assertion was confirmed by the ${}^{31}P{}^{1}H$ NMR spectra recorded for

toluene solutions of the authenticated dimeric species **1a** to which were added various amounts of acetonitrile (Figure 1). These spectra show that portion-wise addition of acetonitrile to the dimeric species (represented by the P singlet at ca. 196.7 ppm) converts it into the monomeric acetonitrile adduct **1a-NCMe** (represented by a new singlet at ca. 193.5 ppm).



Figure 1. ${}^{31}P{}^{1}H$ NMR (162 MHz, 25 mM in PhMe) spectra of 1a upon portion-wise addition of MeCN

The identity of **1a-NCMe** was confirmed by its direct synthesis. which was done as follows. Addition of 10 equiv of MeCN to a suspension of 1a in Et₂O led to an immediate color change from orange to yellow, and evaporation gave the adduct 1a-NCMe as a yellow powder that could be isolated in 86 % yield. The ¹H NMR spectrum of this solid in CD₃CN matched that of 1a in CD₃CN, and the structural assignment was confirmed by single crystal diffraction studies (vide infra). That more than 2 equiv of MeCN are required for a complete transformation of 1a to 1a-NCMe suggests a dimer \leftrightarrows monomer equilibrium (eq. 1). Integration of the 31 P signals for the two species (Figure 1) allowed us to estimate a large equilibrium constant ($K_{eq} \approx ca. 10^3 - 10^4$), which implies a strong preference for the monomeric adduct. A similar conclusion was drawn from the UV-vis spectra recorded for a toluene solution of 1a before and after addition of 10 equiv acetonitrile: the orange solution of the dimer (λ_{max} = 434 nm; $\epsilon_{[Ni]}$ = 737 M⁻¹.cm⁻¹) turned yellow (λ_{max} = 403 nm, $\epsilon_{[Ni]}$ = 1414 $M^{\text{-1}}\text{.cm}^{\text{-1}}$) as a result of the formation of 1a-NCMe. (See Figure S1 for these spectra.) The greater thermodynamic preference for the acetonitrile adduct also explains why it proved difficult to isolate analytically pure samples of the dimer from acetonitrile solutions; indeed, most samples showed the presence of traces of nitrogen (<0.10 %) unless they were subjected to multiple recrystallizations and extended evaporation under vacuum.

Regioselectivity of C-H nickellation with new aryl phosphinites derived from 3-substituted phenols. Having optimized the protocol for the synthesis of 1a, we set out to test our new, acetonitrilebased synthetic protocol for the C-H nickellation of phosphinites derived from substituted phenols. The first substrate we tested was $3-F-C_6H_4OP(i-Pr)_2$ (b) for which cyclonickellation via the toluenebased protocol had given the two regioisomers of *trans*-{{ $\kappa^P, \kappa^C-F-C_6H_4OP(i-Pr)_2$ }Ni{*i*-Pr_2P(OAr)}Br in a 5.6:1 ratio, the major isomer arising from the metallation at the less hindered position (*para* to the C-F moiety.⁶ Applying the new protocol to this phosphinite gave the anticipated dimers with a comparable regioselectivity (Scheme 2).⁹



Scheme 2. Orthonickellation of 3-F-C₆H₄OH in acetonitrile.

Next, we used the acetonitrile-based protocol to expand our investigation of the nickellation regioselectivity beyond 3-F-C₆H₄OH. As shown in Scheme 3, cyclonickellation of aryl phosphinites derived from 3-Me-, 3-MeO-, and 3-Cl-C₆H₄OH occurs exclusively at the *ortho* position farthest from the substituent. Analysis of the reaction mixtures by ³¹P NMR spectroscopy helped signal complete conversion of the starting materials to the nickellated species (singlet at ca. 190–200 ppm), and established the regioselectivities shown in Scheme 3. Work-up furnished the new cyclonickellated species **1c-1e** as orange solids, which were completely characterized by NMR spectroscopy and single crystal diffraction studies; these results will be presented later, following the discussion of the regioselectivity issues.



Scheme 3. Cyclonickellation of 3-substituted and 3,5-disubstituted aryl phosphinites

In light of the observation that the C-H nickellation reactions in question are regioselective regardless of the electron-donating or electron-withdrawing nature of the substituents, we conclude that the main determinant of regioselectivity is sterics, not electronics. This would explain why nickellation is regiospecific with substrates **c** and **e** bearing substituents Me and Cl, respectively, which are of opposite electronic properties but very similar van der Waals

DOI: 10.1039/C7DT03403B Journal Name

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Published on 02 November 2017. Downloaded by University of Reading on 02/11/2017 16:52:12

spherical volumes.¹⁰ Moreover, substrate **b** bearing the smallest non-hydrogen substituent, F, is the only case where the nickellation regioselectivity is less than 100% (6:1).

Cyclonickellation of aryl phosphinites derived from 3,5disubstituted phenols. In order to establish whether the regioselectivities observed with substrates **b-e** reflect a mere *preference* for the least hindered C-H bond, or whether the sterically hindered C-H bond is simply *inaccessible*, we tested the cyclometallation of the disubstituted substrates $3,5-R_2-C_6H_3OP(i Pr)_2$ (R= F (**f**), Me (**g**), Cl (**h**), MeO (**i**)). These tests showed that cyclonickellation occurs with the substrates bearing the smaller substituents F and OMe (**f** in Scheme 3 and **i** in Scheme 4),¹⁰ whereas substrates **g** and **h** bearing the larger Me or Cl substituents did not metallate even after 5 days of heating (Scheme 3).

The above observations confirm the crucial importance of substituent size on C-H nickellation in our system, and suggest that Me and Cl substituents are beyond the steric limits of cyclonickellation. Another noteworthy insight gained from these tests concerns the rate of nickellation, which was quite rapid with the MeO-bearing substrate i and much slower with the F-bearing substrate f (16 vs. 60 h for >90% conversion). A similar trend was evident in the nickellation rates of substrates c and d vs. substrate e (16 vs. 40 h, Scheme 3). These observations are consistent with the presumed electrophilic nature of the C-H nickellation.⁸

Finally, tests conducted on substrate i showed that steric bulk influences not just regioselectivity of C-H nickellation but also the structure of the resulting cyclonickellated product. As shown in Scheme 4, nickellation of substrate i followed by the usual workup failed to give the anticipated μ -Br dimeric species, giving instead the monomeric MeCN adduct 1i-NCMe. This result raised the question of whether the dimeric structure is altogether inaccessible for this substrate, or is it merely less stable for substrate i in comparison to other less bulky substrates. To answer this question, we attempted to drive off the coordinated acetonitrile from the monomeric acetonitrile adduct and generate the putative dimer. However, 1i-NCMe remained unchanged after heating a toluene solution of it to 60 °C and evaporation to dryness under reduced pressure (Scheme 4). This observation indicated that the steric hindrance engendered by the two MeO substituents in substrate i strongly disfavors dimerization of its cyclonickellated derivative, thus favoring the formation of 1i-NCMe.



Scheme 4. Formation of 1i-NCMe from cyclonickellation of i.

 $\label{eq:cyclonickellation of 2-substituted aryl phosphinites. Our investigation of nickellation regioselectivity continued with phosphinites derived from 2-substituted phenols (Scheme 5). We first examined the reaction of {($ *i* $-PrCN)NiBr_2}_n with phosphinite$ **j**

(derived from *ortho*-cresol) to test if nickellation at the C_{sp3} -H of the 2-Me substituent might be competitive with the anticipated *ortho*-nickellation at the unsubstituted position. The results confirmed, however, exclusive reactivity at the unsubstituted *ortho*-C-H position. That the outcome of this reaction is not necessarily due to the intrinsically more favorable nickellation of sp^2 vs sp^3 C-H moieties was inferred from the nickellation of phosphinite **k** (derived from 2-phenylphenol), which also occurred at the unsubstituted *ortho*-C-H position of the main aryl ring and not the sp^2 C-H moiety of the substituent (Scheme 5).



Scheme 5. Cyclonickellation of various mono- or di-orthosubstituted aryl phosphinites.

The above-discussed reactivity, i.e., exclusive nickellation at the unsubstituted ortho-C-H position of the phenol ring as opposed to the C-H moiety of the methyl or phenyl substituent, is presumably a result of the more favorable energetics of the 5-membered metallacycles that form at the transition state versus the alternative 6- or 7-membered metallacycles. Comparison of these results to related literature reports reveals that the regioselectivity under discussion is a function of the metal precursor; it also depends on whether the substrate ArOH is derivatized or not. For instance, using a Rh(I) pre-catalyst along with ArOPR₂ leads to metallation/coupling with aryl halides at the ortho-C-H of both the main ring (5-membered metallacycle) and the Ph substituent at the metallacycle),¹¹ position (7-membered whereas ortho metallation/coupling of underivatized 2-aryl phenols with Pd(OAc)₂/Cs₂CO₃ as pre-catalyst occurs only at the ortho-C-H of the Ph substituent (6-membered metallacycle).¹²

Two other reactions were carried out with ligands bearing substituents at both ortho positions to test if nickellation can be forced on a substituent C-H site. Thus, reactions with ligands I (derived from 2,4,6-Me₃-C₆H₂OH)¹³ and **m** (derived from 2,6-Ph₂- C_6H_3OH) were examined, but neither showed any nickellation even after 5 days of heating. To establish whether this lack of reactivity is due to the inability of these phosphinites to coordinate to the Ni center, we examined the reactivity of the Ni precursor with two equivalents of ligand m in the absence of added base. Similarly to what had been observed with all other less hindered phosphinites, no coordination was observed at r.t., but heating the reaction mixture to 80 °C for one hour led to a brownish mixture that showed a new ³¹P resonance at 134 ppm, which is in a region characteristic of the bis-phosphinite complexes trans-(i-Pr₂POAr)₂NiBr₂. We conclude that sterically hindered phosphinites can coordinate to Ni(II), at least in the absence of other nucleophiles. This implies in turn that the observed failure to induce

	Ni-C	Ni-P	<i>trans</i> -Ni-Br ^b	<i>cis</i> -Ni-L ^b	C-Ni-P	Br-Ni-L	Ni-Br-Ni	NiNi	τ4
1a	1.914(4)	2.095(1)	2.377	2.3641(7)	82	88	92	3.415	0.059
1b	1.911(4)	2.106(1)	2.3736(8)	2.3781(7)	84	87	83	3.164	0.056
1c	1.920(3)	2.0963(7)	2.390	2.3815(5)	82	88	92	3.444	0.042
1d ^c	1.914(2); 1.88(3); 1.95(3)	2.0985(5); 2.0972(5)	2.3803(3); 2.3851(3)	2.3857(3); 2.3875(3)	79; 83; 87	87	76	2.9406(3)	0.052; 0.113; 0.116
1e	1.914(2)	2.0987(7)	2.382	2.3796(5)	82	88	92	3.436	0.036
1f	1.931(2)	2.1017(5)	2.3743(3)	2.386	82	86	94	3.485	0.102
1j	1.911(2)	2.0936(4)	2.3759(3)	2.392	83	87	93	3.444	0.059
1k ^d	1.894(10)– 1.926(10)	2.098(3)– 2.105(3)	2.357(2)– 2.389(2)	2.387(2)– 2.398(2)	81–83	86–87	93–94	3.458– 3.471	0.030– 0.084
1a-NCMe	1.916(2)	2.1018(6)	2.3533(4)	1.913(2)	83	91	-	-	0.074
1i-NCMe	1.932(2)	2.1000(6)	2.3613(4)	1.915(2)	83	91	-	-	0.204

 Table 1. Selected structural parameters for dimers and MeCN adducts.^a

a) The values for angles have been rounded up to the nearest degree. b) Designation of *cis*- and *trans*-Ni-Br bonds is with respect to the Ni-C2 bond. c) In this nonsymmetrical structure, two different values are observed for all parameters except the Ni-C distance and C-Ni-P angle for which three different values are observed due to the presence of disorder in one half of the dimer. d) These ranges represent the bond distances and angles observed in the four molecules present in the asymmetric unit.

C-H nickellation in disubstituted ligands I and m, even after extended heating, likely reflects the strong energetic preference for transition states leading to formation of 5-membered nickellacycles. **Solid state structures of the new complexes.** Solid state structures were determined for 9 new cyclonickellated complexes, of which two are monomeric adducts and 7 dimers. The results of these analyses allowed us to unequivocally establish the identities of all complexes. In the case of complex **1k**, resolution of the structural data was problematic due to the twinned crystals obtained;¹⁴ hence, structural discussion in this case will be limited to those features that are established with confidence. The pertinent structural parameters for all complexes are listed in Table 1 and Tables S2–S3, the molecular drawings are shown in Figures 2–5 and Figures S86–S90, and the main findings are discussed below.

Complex 1a-NCMe (Figure 2), the mononuclear acetonitrile adduct obtained from cyclonickellation of unsubstituted phosphinite a, showed a fairly unremarkable solid state structure in which the largest distortion is the smaller-than-ideal bite angle of the metallated phosphinite moiety (ca. 83°). By comparison, relatively major angular distortions were noted in the analogous monomeric adduct 1i-NCMe obtained from nickellation of the phosphinite derived from 3.5-methoxy-phenol (Figure 2). Thus, the two trans angles are compressed to ca. 166° and 164°, and the C-Ni-N cis angle is enlarged to 100°. These non-ideal angles translate into a much more pronounced tetrahedral distortion in 1i-NCMe vs. 1a-**NCMe**, as reflected in τ_4 values of 0.20 and 0.07, respectively.¹⁵ We conclude, therefore, that the presence of a non-hydrogen substituent vicinal to the nickellation site distorts the solid state structure of these complexes. In the crystal structures of the dimeric species 1b-1f, 1j, and 1k (Figures 3–5 and S86–S90), both Ni centers adopt nearly ideal square planar geometries, indicating that neither the steric bulk nor the substituent position has any significant bearing on the overall coordination geometry of the dimeric complexes. To be sure, some degree of tetrahedral distortion is evident in all dimeric complexes studied here, but these are fairly insignificant as can be deduced from the small τ_4 values that define these distortions15 (0.03 to 0.12; Tables 1 and S2–S3). It should also be noted here that the presence in **1f** of an F substituent vicinal to the nickellation site causes little distortion (τ_4 = 0.102), whereas major structural distortions are evident in **1i**-**NCMe** due to the presence of MeO (*vide supra*). This difference is likely a reflection of the smaller van der Waals volume of F compared to that of MeO.

The nature of the substituents also has little or no impact on bond distances found in the dimeric complexes: the values for Ni-P (2.094–2.106 Å), Ni-C (1.911–1.931 Å), and Ni-Br (2.374–2.393 Å) fall within the normal range for related Ni(II) complexes. Comparing these values to the corresponding distances in the related resorcinol-based pincer complexes (R_n -POCOP^{*i*-Pr})NiBr reveals that the cyclonickellated compounds under discussion here feature somewhat longer distances for Ni-C (1.91 vs 1.89 Å) and Ni-Br(2.36-2.39 vs 2.323 Å), but slightly shorter P-Ni bond distances (2.10 vs 2.142/2.153 Å).¹⁶

One unexpected and fairly significant structural distortion that was observed in some dimeric complexes regards the relative spatial orientations of the two halves of these molecules. As expected, dimers possessing an inversion center adopt a structure wherein the two halves of the dimer are coplanar, whereas dimers that do not crystallize on an inversion center display various degrees of deviation from co-planarity. The extent of the "bending" of the two halves of the dimers is conveniently quantified by the torsion angles Dalton Transactions

DOI: 10.1039/C7DT03403B Journal Name



Figure 2. Top views of the molecular diagrams for complexes 1a-NCMe (left) and 1i-NCMe (middle), and side view for complex 1i-NCMe (right). Thermal ellipsoids are shown at the 50% probability level. Hydrogens in all diagrams and Me groups in the side view of 1i-NCMe have been omitted for clarity.

Ni1- μ -Br1- μ -Br2-Ni2 atoms, which would be 180° in a coplanar arrangement (no bending at all). The measured values of this torsion angle ranged from ca. 170–172°¹⁷ in **1k** to ca. 133° in **1b** and ca. 116° in **1d**. One consequence of the "bending" represented by the torsion angles for **1b** and **1d** is a shrinking of the Ni-Br-Ni angle, which is 83° in **1b** and 76° in **1d**, compared to angles of \geq 92° in all coplanar dimers. A potentially even more significant structural consequence of the bending is that it brings the two Ni centers closer to each other; thus, the Ni---Ni distances are 3.16 Å in **1b** and 2.94 Å in **1d**, compared to > 3.4 Å in coplanar dimers.

Of course, such shortened distances do not necessarily imply bonding interactions as they are still longer than the sum of covalent radii for two Ni(II) atoms (≈ 2.50 Å)¹⁸, but they are still shorter than the sum of two van der Waals radii (≈ 3.26 Å).

Indeed, such interactions would be rather surprising given that the filled d_{z^2} orbitals in these d^8 centers are expected to favor a conformation that would minimize any orbital interactions. On this basis alone, a coplanar conformation (torsion angle = 180°) would have been optimal in the absence of packing forces.





Figure 3. Top and side views of the molecular diagram for complex **1d**. Thermal ellipsoids are shown at the 50% probability level; hydrogens in both views and the *P*-substituents in the side view have been omitted for clarity.

Figure 4. Top view of the molecular diagram for complex **1f** and side view for a portion of the dimer. Thermal ellipsoids are shown at the 50% probability level; hydrogens are omitted for clarity. The side view shows the ligands around only one Ni atom.

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Figure 5. Top view of the molecular diagram for complex 1k. Thermal ellipsoids are shown at the 50% probability level; hydrogens are omitted for clarity.

We have probed this phenomenon using DFT calculations to identify the optimal geometries for the dimeric complex **1d** in toluene. All optimizations were carried out using Gaussian 16 with M06 functional method in implicit toluene solvent using the SMD model. The experimentally obtained solid state structure for **1d** was used as the beginning point for the first geometry optimizations; these led to a bent structure featuring Ni---Ni bond distances and torsion angles very similar to those found in the solid state structure (ca. 2.75 Å vs. 2.94 Å; 102° vs 116° respectively). The geometry was then allowed to unfold to a structure displaying a coplanar conformation around Ni1-Br1-Br2-Ni2. Optimization of this coplanar geometry led to a local minimum, which was found to be less stable than the bent structure: $\Delta G^{\circ}_{bending} = -6.5$ kJ/mol.

DFT optimizations were also applied to **1a**, the parent dimer that crystallizes on an inversion center and hence adopts a coplanar structure in the solid state. In this case, too, the planar structure obtained after initial optimizations appeared to be only a local minimum, because optimizations carried out on starting structures featuring non-coplanar Ni₂Br₂ cores led to a bent geometry that was more stable relative to the coplanar structure: torsion angle of 104°; Ni---Ni bond distance of ca. 2.77 Å; Δ G°_{bending} = -5.7 kJ/mol.

In order to avoid local minima resulting from the different possible orientations of the *i*-Pr groups in the $P(i-Pr)_2$ moieties, further optimizations were carried out on the PMe₂ analogues of **1a** and **1d**. As a further measure for ensuring the reliability of our optimization studies, the PMe₂ analogue of **1d** was allowed to adopt the three possible conformations due to the two orientations of the MeO substituents observed in the crystal structure of **1d**. (See SI for details of these structures.) In all four cases, optimizations generated bent structures for these PMe₂ analogues of **1a** and **1d**, with structural parameters very similar to those seen in the solid state structure of the $P(i-Pr)_2$ complexes: torsion angles $\approx 100-103^\circ$; Ni---Ni distances $\approx 2.68-2.70$ Å. As before, freezing the torsion angles at 180° (coplanar structures) followed by optimization yielded a local minimum for each structure, but these were always less stable than the bent ones by 1.3-3.8 kJ/mol.

Altogether, the results of our DFT studies imply that this family of dimeric Ni(II) complexes must have an intrinsic preference for adopting non-coplanar conformations. As a result, non-coplanar conformations are found in the solid state unless there is a crystallographic inversion center in the unit cell. The underlying

causes for this preference for bent conformations cannot be identified at this point. Indeed, it is still unclear whether this tendency is driven by stabilizing interactions between the two d⁸ centers, or whether the shortened Ni---Ni distances observed are simply the consequence of the bending, as opposed to being its cause. What seems clear at this point is that no simple correlation exists between the degree of bending and Ni---Ni distances in complexes studied, on the one hand, and the electron-withdrawing or -releasing properties of their ring substituents (3-F, 3-MeO) on the other. This phenomenon will be probed in future investigations.

NMR characterization of the cyclonickellated dimers. All attempts to record informative NMR spectra using CDCl₃, CD₂Cl₂, or C₆D₆ solutions of the dimeric complexes resulted in poorly resolved spectra featuring low signal-to-noise ratios. In contrast, CD₃CN solutions gave high-quality spectra that facilitated solution characterization of these complexes. This difference in the spectral quality as a function of solvent nucleophilicity is presumably due to a relatively slow dynamic process occurring in non-nucleophilic solvents (e.g., the flipping up and down of the dimer), whereas complete dissociation of the dimers takes place in acetonitrile to give monomeric acetonitrile adducts that do not experience this fluxionality.¹⁹ To shed some light on this issue, we carried out a computational study to estimate the energy barrier required for the flipping motion of a simplified model (Me₂P instead of *i*-Pr₂) for the bent dimer 1a. (See SI for technical details on this study.) The energy barrier obtained for flipping 1a-PMe₂ via a coplanar transition state was only 11.6 kJ/mol, which is easily accessible at room temperature. This result implies that the relatively slow up and down flipping of dimers in solution might well be the cause of the poorly-resolved NMR spectra alluded to above.²⁰ Regardless of the precise reason(s) for these observations, it should be emphasized that the well-resolved spectra discussed below are those of the monomeric acetonitrile adducts { κ^{P} , κ^{C} -R-ArOP(*i*- $Pr_{2}NiBr(NCCD_{3})$ derived from each dimer.

The ³¹P{¹H} NMR spectra recorded for the CD₃CN samples of all dimers displayed a singlet resonance at 190-198 ppm. The corresponding ¹H NMR spectra were also consistent with the loss of one aromatic proton as a result of nickellation, and featured the characteristic signals for i-Pr protons (two dd for the diastereotopic Me groups, and a pseudo-octuplet for the methyne C-H). For the dimeric complex 1f, the assignments of the H-P and H-F couplings were facilitated thanks to the selectively decoupled ¹H{³¹P} and ¹H{¹⁹F} spectra (See Figures 6 and S50–S52). Further evidence for nickellation was also obtained from the ¹³C{¹H} NMR spectra featuring doublets at 105 - 130 ppm (${}^{2}J_{CP} = 30-40$ Hz) and 160-168ppm $({}^{2}J_{CP} = 11-15 \text{ Hz})$ for the nickellated carbon C2 and the Obearing carbon C1, respectively. In some cases, P-C coupling was also visible for other aromatic carbons, but these showed generally much smaller coupling constants (${}^{3}J_{CP}$ and ${}^{4}J_{CP} < 5$ Hz). The NMR spectra of the CD3CN solutions of dimers 1b/1b', 1f, and 1k showed particularly intriguing coupling patterns and provided a wealth of information about the various coupling interactions.

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Very informative coupling patterns were also observed in the spectra recorded for 1k/CD₃CN, the complex derived from 2phenylphenol. For instance, a singlet was observed for C10 (the para position on Ph substituent), whereas two doublets were found for C8/12 and C9/11 (the ortho- and meta-C nuclei on the Ph substituent) featuring unusually large couplings due to dipolar coupling to the ³¹P nucleus (J_{CP} = 107 and 140 Hz, respectively). Assignments of C8/12 and C9/11 for the 2-Ph substituent were confirmed by HSQC experiments. The signals for the guaternary carbons C6 and C7 were not detected at all.

Conclusions

The following are the main findings of this study with respect to C-H nickellation regioselectivity: (a) the aryl phosphinites *i*-Pr₂POAr undergo C-H nickellation when heated in acetonitrile solutions containing the nickel precursor [(*i*-PrCN)NiBr₂]_n and NEt₃, giving the acetonitrile adducts trans-{ κ^{P} , κ^{C} -ArOP(*i*-Pr)₂}Ni(NCMe)Br that upon work-up yield the dimeric species $\{\kappa^{P}, \kappa^{C}-ArOP(i-Pr)_{2}\}_{2}Ni_{2}Br_{2}$ for every substrate tested except that with Ar= $3,5-(OMe)_2-C_6H_3$ that gave the acetonitrile adduct { κ^{P} , κ^{C} -3,5-(OMe)₂-C₆H₃ OP(*i*-Pr)₂}NiBr(NCMe); (b) the C-H nickellation of all but one of the phosphinites derived from 3-R-C₆H₄OH occurs regioselectively at the less hindered ortho position, the only exception being observed with substrate (3-F-C₆H₄O)P(*i*-Pr)₂ that gives a 6:1 mixture of regioisomers (major one nickellated at the less hindered ortho position); (c) the C-H nickellation of both phosphinites derived from 2-R-CH₄OH (R= Me, Ph) also occurs regioselectively at the only available ortho C-H of the phenol ring, not at the substituent C-H moiety; (d) no C-H nickellation occurs with the disubstituted phosphinites derived from 2,6-R₂-C₆H₃OH (R= Me, Ph), whereas for those derived from 3,5-R₂-C₆H₃OH C-H nickellation was possible with R= F or OMe but not Me or Cl.

The above results indicate that the reactivity with 3-substituted is highly sensitive to the steric size of the phenol substituent(s), nickellation occurring exclusively or preferentially at the less congested site, whereas C-H nickellation with the 3,5-disubstituted substrates is altogether inaccessible with the substituents Me and Cl. Another important factor is the size of the resulting nickellacycles: the greater preference for a 5-membered nickellacycle precludes nickellation at the phenol substituent C-H sites in 2-substituted and 2,6-disubstitued substrates.

Other interesting findings of this study include the confirmation of a previously noted observation that C-H nickellation of these substrates occurs more readily with electron-rich substrates (R = Me, OMe), and also the observation that the dimers adopt more stable bent conformations and they break apart into monomeric adducts in the presence of even weakly nucleophilic reagents such as acetonitrile. This latter reactivity should open the way to potentially interesting functionalization pathways, which we intend to explore. Our future studies will also focus on elucidating the mechanism of C-H nickellation.

Figure 6. Aromatic region of the ${}^{1}H$, ${}^{1}H$ { ${}^{19}F$ }, and ${}^{1}H$ { ${}^{31}P$ } NMR spectra of **1f**, disclosing J_{HF} , J_{HH} and J_{HP} couplings.

For example, the ¹⁹F NMR spectrum for the mixture of the two regioisomers 1b and 1b' displayed a pseudo-quartet at -118 ppm for the major isomer with para-F (${}^{3}J_{HF} \approx {}^{4}J_{HF} \approx 9$ Hz) and a doublet of doublets at -95 ppm for the minor isomer with ortho-F (${}^{3}J_{HF} = 9$ Hz, ${}^{4}J_{HF}$ = 6 Hz). Correlating these chemical shifts with those of the two ¹⁹F resonances found at δ -116.4 (q, ${}^{3}J_{HF} = {}^{3}J_{H'F} = {}^{4}J_{FF} = 9$ Hz) and -93 (t, ${}^{3}J_{HF} = {}^{4}J_{FF} = 9$ Hz) for dimer **1f** allowed an unambiguous identification of the two F nuclei.

The ${}^{13}C$ NMR spectrum of **1f**/NCCD₃ was also quite informative: two ¹³C doublets of doublets featuring large ${}^{1}J_{FC}$ coupling constants (ca. 240 Hz) were readily attributed to the two F-bearing carbon nuclei C5 and C3 (see Figure S53 in SI). However, the doublets in question did not display any J_{C-P} coupling, which precluded their assignment to the specific nuclei C3 and C5. On the other hand, the data allowed exact assignments for the remaining carbon nuclei of the aromatic ring in **1f**. Thus, C2 and C6 showed (Figure 7) both ${}^{2}J_{CP}$ (39 Hz) and ${}^{3}J_{CP}$ (13 Hz) as well as ${}^{2}J_{CF}$ (ca. 36 and 24 Hz, respectively) and even ${}^{4}J_{CF}$ coupling constants (ca. 3 and 4 Hz, respectively). A ddd 13 C resonance at 168 ppm was attributed to C1 (${}^{3}J_{CF}$ = 25 Hz; ${}^{3}J_{CF'}$ = 14 Hz; ${}^{2}J_{CP}$ = 11 Hz), while another ddd was observed for C4 and attributed to two different ${}^{2}J_{CF}$ couplings: 36 and 25 Hz. Finally, it is noteworthy that we observe P-C6 coupling but no P-H6 coupling, whereas the opposite is the case for C4, i.e., we observe P-H4 coupling but no P-C4 coupling



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Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

The authors gratefully acknowledge financial support provided by: NSERC of Canada (Discovery grants to D.Z.); Centre in Green Chemistry and Catalysis (CGCC/CCVC, summer research stipends and travel awards); Université de Montréal (graduate scholarships to L. P. M.). We also thank our colleagues, Dr. M. Simard (for help with the resolution of the solid state structure for complex **1k**), Prof. F. Schaper (for valuable advice on the refinement of this structure), and Mr. J.-P. Cloutier (for discussions with regards to the DFT studies). Finally, Compute Canada-Calcul Canada is acknowledged for access to Westgrid Computational Facilities.

Experimental section

General considerations. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques and an inert-atmosphere box. The solvents were dried by passage over a column of activated alumina, collected under nitrogen, and stored over 4 Å molecular sieves. Triethylamine was dried over CaH₂. Synthesis of the nickel precursor {(*i*-PrCN)NiBr₂}_n used throughout this study has been described previously.²¹ 3,5-dichlorophenol was synthesized from demethylation of 3,5-dichloroanisole in refluxing 48 % aq. HBr. All other reagents were purchased from Sigma-Aldrich and used without further purification.

Unless otherwise specified, all 1D NMR spectra were recorded at 500 MHz (¹H), 125.72 MHz (¹³C), 202.4 MHz (³¹P) and 470.4 MHz (¹⁹F), whereas the HSQC experiments were recorded at 400 MHz (¹H) and 100.6 MHz (¹³C). Chemical shift values are reported in ppm (δ) and referenced internally to the residual solvent signals (¹H and ¹³C: 1.94 and 118.26 ppm for CHD₂CN) or externally (³¹P, H₃PO₄ in D₂O, δ = 0; ¹⁹F, CFCl₃, δ = 0). The values for *J* coupling are given in Hz. The NMR data obtained for CD₃CN solutions of the dimeric complexes correspond to the corresponding monomeric NCCD₃ adducts.

General procedure for the synthesis of cyclonickellated phosphinite dimers. To a solution of ArOH (2.00 mmol) in 20 mL dry THF was added Et₃N (2.20 mmol, 307 μ L, 1.10 equiv) and then CIP(*i*-Pr)₂ (2.10 mmol, 334 μ L, 1.05 equiv) after which salt precipitation started. The mixture was stirred at room temperature until the reaction was complete (from 0.5 to 20 h, as monitored by ³¹P NMR). The solvent was removed under vacuum, the residues extracted with Et₂O (3x15 mL), and evaporated to yield a colourless to pale yellow oil. To the latter was added dry MeCN (20 mL), {(*i*-PrCN)NiBr₂}_n (2.40 mmol, 691 mg, 1.2 equiv), and Et₃N (2.40 mmol, 335 μ L, 1.2 equiv). The resulting green to brownish-green homogeneous mixture was stirred at 80 °C until the reaction was complete (monitored by the disappearance of the starting material ³¹P signal at *ca*. 135 ppm). The solvent was then removed under

vacuum and the residues were extracted with toluene by filtration through Celite[®]. The toluene was removed under vacuum and the residues (deliquescent solids or dark orange pasty products) were dissolved in a minimum of Et₂O, precipitated with hexanes, filtered off and the solids washed with a minimum of hexanes to complete removal of impurities. The remaining solid was dried under vacuum to yield a bright to dull orange powder. Single crystals were obtained by slow evaporation of an Et₂O solution kept under N₂.

 $[\{\kappa^{P}, \kappa^{C} - (i-Pr)_{2}PO - C_{6}H_{4}\}Ni(\mu-Br)]_{2}$ (1a). This compound has been synthesized previously via a different procedure.6 The revised general procedure described above was applied on a 5.00 mmol scale in MeCN over 16 h at 80 °C. Yield of the bright orange powder obtained: 1.514 g (2.17 mmol, 87 %). The NMR spectroscopic data in CD₃CN confirmed the identity of the compound. ¹H NMR (500 MHz, 20 °C, CD₃CN): δ 1.31 (dd, 6H, CH(CH₃)(CH₃), ³J_{HH} = 7.0, ³J_{HP} = 14.9), 1.46 (dd, 6H, CH(CH₃)(CH₃), ${}^{3}J_{HH} = 7.2$, ${}^{3}J_{HP} = 17.5$), 2.44 (oct, 2H, CH(CH₃)₂, ${}^{3}J_{HH} \approx {}^{2}J_{HP} = 7.1$), 6.63 (dd, 1H, C6_{Ar}-H, ${}^{3}J_{HH} = 7.9$, ${}^{4}J_{HH} =$ 1.3), 6.68 (tt, 1H, C4_{Ar}-H, ${}^{3}J_{HH} = 7.4$, ${}^{4}J_{HH} \approx {}^{5}J_{HP} = 1.1$), 6.98 (tm, 1H, $C5_{Ar}-H$, ${}^{3}J_{HH} = 7.5$, ${}^{4}J_{HH} = 1.4$), 7.16 (dt, 1H, $C3_{Ar}-H$, ${}^{3}J_{HH} = 7.6$, ${}^{4}J_{HH} \approx$ ${}^{4}J_{HP}$ = 1.4). ${}^{13}C{}^{1}H{}$ NMR (125.7 MHz, 20 °C, CD₃CN): δ 16.88 (d, 2C, $CH(CH_3)(CH_3)$, ${}^{2}J_{CP} = 1.9$, 18.50 (d, 2C, $CH(CH_3)(CH_3)$, ${}^{2}J_{CP} = 2.7$), 29.07 (d, 2C, CH(CH₃)(CH₃), ¹J_{CP} = 29.0), 110.60 (d, 1C, C6_{Ar}-H, ³J_{CP} = 13.2), 121.43 (d, 1C, $C4_{Ar}$ -H, ${}^{4}J_{CP}$ = 2.0), 127.56 (s, 1C, $C5_{Ar}$ -H), 133.78 (d, 1C, $C2_{Ar}$ -Ni, $^{2}J_{CP}$ = 33.9), 139.11 (d, 1C, $C3_{Ar}$ -H, $^{3}J_{CP}$ = 2.6), 167.66 (d, 1C, *C1*_{Ar}-OP, ²*J*_{CP} = 11.9). ³¹P{¹H} NMR (202.4 MHz, 20 °C, CD₃CN): δ 196.21 (s, 1P).

 $[{\kappa^{P}, \kappa^{C} - (i-Pr)_{2}PO - (5-F-C_{6}H_{3})}Ni(\mu-Br)]_{2}$ (1b) and $[(\kappa^{P}, \kappa^{C} - (i-Pr)_{2}PO - (3-F)]_{2}$ $F-C_6H_3$)Ni(μ -Br)]₂ (1b'). Applying the general procedure given above (at 80 °C for 36 h) gave a bright orange powder. Yield: 382 mg (0.522 mmol). This solid was shown by ${}^{31}P{}^{1}H{}$ and ${}^{19}F$ NMR spectra to contain the two isomers 1b (major, metallated para to F) and 1b' (minor, metallated ortho to F) in a 6.5 : 1 ratio. Spectroscopic data for **1b** :¹H NMR (500 MHz, 20 °C, CD₃CN): δ 1.30 (dd, 6H, $CH(CH_3)(CH_3)$, ${}^{3}J_{HH} = 7.2$, ${}^{3}J_{HP} = 15.1$), 1.46 (dd, 6H, $CH(CH_3)(CH_3)$, ${}^{3}J_{HH}$ = 7.2, ${}^{3}J_{HP}$ = 17.6), 2.44 (oct, 2H, CH(CH₃)₂, ${}^{3}J_{HH} \approx {}^{2}J_{HP}$ = 7.2), 6.45 (dd, 1H, $C6_{Ar}$ -H, ${}^{3}J_{HF}$ = 10.2, ${}^{4}J_{HH}$ = 2.6), 6.48 (tdd, 1H, $C4_{Ar}$ -H, ${}^{3}J_{HH} \approx {}^{3}J_{HF}$ = 9.4, ${}^{4}J_{HH} = 2.7$, ${}^{5}J_{HP} = 0.9$), 7.11 (tm, 1H, C3_{Ar}-H, ${}^{3}J_{HH} \approx {}^{4}J_{HF} = 7.3$, ${}^{4}J_{HP} =$ 0.8). ¹³C{¹H} NMR (125.7 MHz, 20 °C, CD₃CN): δ 18.04 (d, 2C, $CH(CH_3)(CH_3)$, ${}^{2}J_{CP} = 1.9$, 18.65 (d, 2C, $CH(CH_3)(CH_3)$, ${}^{2}J_{CP} = 2.7$), 29.34 (d, 2C, CH(CH₃)(CH₃), ${}^{1}J_{CP}$ = 29.0), 98.89 (dd, 1C, C6_{Ar}-H, ${}^{2}J_{CF}$ = 24.7, ${}^{3}J_{CP}$ = 13.9), 108.01 (dd, 1C, $C4_{Ar}$ -H, ${}^{2}J_{CF}$ = 19.6, ${}^{4}J_{CP}$ = 1.7), 128.20 (d, 1C, $C2_{Ar}$ -Ni, $^{2}J_{CP}$ = 34.2), 139.60 (dd, 1C, $C3_{Ar}$ -H, $^{3}J_{CF}$ = 8.5, ${}^{3}J_{CP}$ = 3.1), 163.53 (d, 1C, $C5_{Ar}$ -F, ${}^{2}J_{CF}$ = 240.8), 167.84 (dd, 1C, $C1_{Ar}$ -OP, ${}^{3}J_{CF}$ = 13.2, ${}^{2}J_{CP}$ = 11.2). ${}^{31}P{}^{1}H}$ NMR (202.4 MHz, 20 °C, CD₃CN): δ 197.72 (s, 1P). ¹⁹F NMR (470.4 MHz, 20 °C, CD₃CN): δ -118.39 (q, 1F, $C5_{AF}$ -*F*, ${}^{3}J_{HF} \approx {}^{4}J_{HF} = 9.4$). Spectroscopic data for **1b'** : ¹H NMR (500 MHz, 20 °C, CD₃CN): δ 1.30 (dd, 6H, CH(CH₃)(CH₃), ${}^{3}J_{HH} = 7.2$, ${}^{3}J_{HP} =$ 15.1), 1.47 (dd, 6H, CH(CH₃)(CH₃), ³J_{HH} = 7.1, ³J_{HP} = 17.7), 2.44 (oct, 2H, CH(CH₃)₂, ${}^{3}J_{HH} \approx {}^{2}J_{HP} = 7.2$), 6.38 (1H, tm, C4_{Ar}-H, ${}^{3}J_{HH} \approx {}^{3}J_{HF} = 8.5$, ${}^{4}J_{HH}$ = 1.1), 6.51 (1H, dd, C6_{Ar}-H, ${}^{3}J_{HH}$ = 7.9, ${}^{4}J_{HH}$ = 1.1), 6.98 (1H, qm, $C5_{Ar}-H$, ${}^{3}J_{HH} = 7.9$, ${}^{4}J_{HF} = 6.2$, ${}^{5}J_{HP} = 1.1$). ${}^{13}C{}^{1}H$ NMR (125.7 MHz, 20 °C, CD₃CN): δ 18.09 (d, 2C, CH(CH₃)(CH₃), ²J_{CP} = 2.2), 18.78 (d, 2C, $CH(CH_3)(CH_3)$, ${}^{2}J_{CP} = 2.2$), 29.75 (d, 2C, $CH(CH_3)(CH_3)$, ${}^{1}J_{CP} = 30.0$), 107.40 (dd, 1C, $C6_{Ar}$ -H, ${}^{3}J_{CP}$ = 12.2, ${}^{4}J_{CF}$ = 2.6), 109.24 (dd, 1C, $C4_{Ar}$ -H,

DOI: 10.1039/C7DT03403B

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Published on 02 November 2017. Downloaded by University of Reading on 02/11/2017 16:52:12

³*J*_{CF} = 29.7, ⁴*J*_{CP} = 1.4), 128.91 (d, 1C, *C5*_{Ar}-H, ³*J*_{CF} = 10.2), 168.82 (m, 1C, *C1*_{Ar}-OP), 171.68 (d, 1C, *C3*_{Ar}-F, ¹*J*_{CF} = 238.8), *C2*_{Ar}-Ni was not detected. ³¹P{¹H} NMR (202.4 MHz, 20 °C, CD₃CN): δ 192.04 (s, 1P). ¹⁹F NMR (470.4 MHz, 20 °C, CD₃CN): δ -95.55 (dd, 1F, C3_{Ar}-*F*, ³*J*_{HF} = 9.3, ⁴*J*_{HF} = 6.2). Anal. Calc. for C₂₄H₃₄F₂O₂P₂Ni₂Br₂: C, 39.40; H, 4.68. Found: C, 38.61; H, 4.86; N, 0.24.

[{\kappa^{P}, \kappa^{L}-(*i***-Pr)₂PO-(5-Me-C₆H₃)}Ni(μ-Br)]₂ (1c).** Applying the general procedure given above (at 80 °C for 16 h) gave a dull orange powder. Yield: 487 mg (0.673 mmol, 67%). ¹H NMR (500 MHz, 20 °C, CD₃CN): δ 1.29 (dd, 6H, CH(CH₃)(CH₃), ³J_{HH} = 7.0, ³J_{HP} = 14.9), 1.45 (dd, 6H, CH(CH₃)(CH₃), ³J_{HH} = 7.2, ³J_{HP} = 17.5), 2.19 (s, 3H, Ar-CH₃), 2.42 (oct, 2H, CH(CH₃)₂, ³J_{HH} \approx ²J_{HP} = 7.2), 6.49 (s, 1H, C6_{Ar}-H), 6.52 (d, 1H, C4_{Ar}-H, ³J_{HH} = 7.8), 7.01 (d, 1H, C3_{Ar}-H, ³J_{HH} = 7.8), ¹³C{¹H} NMR (125.7 MHz, 20 °C, CD₃CN): δ 17.75 (d, 2C, CH(CH₃)(CH₃), ²J_{CP} = 1.8), 18.37 (d, 2C, CH(CH₃)(CH₃), ²J_{CP} = 2.8), 20.46 (s, 1C, Ar-CH₃), 28.87 (d, 2C, CH(CH₃)(CH₃), ¹J_{CP} = 1.8), 122.24 (d, 1C, C4_{Ar}-H, ⁴J_{CP} = 1.8), 129.33 (d, 1C, C2_{Ar}-Ni, ²J_{CP} = 34.4), 137.59 (s, 1C, C5_{Ar}-Me), 138.64 (d, 1C, C3_{Ar}-H, ³J_{CP} = 2.7), 167.50 (d, 1C, C1_{Ar}-OP), ²J_{CP} = 12.3). ³¹P{¹H} NMR (202.4 MHz, 20 °C, CD₃CN): δ 195.79 (s, 1P). Anal. Calc. for C₂₆H₄₀O₂P₂Ni₂Br₂: C, 43.15; H, 5.57. Found: C, 42.88; H, 5.69; N, 0.03.

 $[{\kappa}^{P}, \kappa^{C}-(i-Pr)_{2}PO-(5-MeO-C_{6}H_{3})]Ni(\mu-Br)]_{2}$ (1d). Applying the general procedure given above (at 80 °C for 16 h) gave a dull orange powder. Yield: 452 mg (0.598 mmol, 60%). ¹H NMR (500 MHz, 20 °C, CD₃CN): δ 1.30 (dd, 6H, CH(CH₃)(CH₃), ³J_{HH} = 7.1, ³J_{HP} = 14.9), 1.45 (dd, 6H, CH(CH₃)(CH₃), ${}^{3}J_{HH} = 7.2$, ${}^{3}J_{HP} = 17.5$), 2.42 (oct, 2H, $CH(CH_3)_2$, ${}^{3}J_{HH} \approx {}^{2}J_{HP} = 7.2$), 3.69 (s, 3H, Ar-OCH₃), 6.28 (d, 1H, C6_{Ar}-H, ${}^{4}J_{\rm HH}$ = 2.6), 6.31 (ddd, 1H, C4_{Ar}-*H*, ${}^{3}J_{\rm HH}$ = 8.5, ${}^{4}J_{\rm HH}$ = 2.6, ${}^{5}J_{\rm HP}$ = 0.9), 7.00 (dd, 1H, $C3_{Ar}-H$, $^{3}J_{HH} = 8.5$, $^{4}J_{HH} = 1.0$). $^{13}C{^{1}H}$ NMR (125.7 MHz, 20 °C, CD₃CN): δ 16.85 (d, 2C, CH(CH₃)(CH₃), ²J_{CP} = 2.0), 18.47 (d, 2C, $CH(CH_3)(CH_3)$, ${}^{2}J_{CP} = 2.8$), 28.98 (d, 2C, $CH(CH_3)(CH_3)$, ${}^{1}J_{CP} = 28.8$), 55.45 (s, 1C, Ar-OCH₃), 97.42 (d, 1C, $C6_{Ar}$ -H, ${}^{3}J_{CP}$ = 14.0), 107.28 (d, 1C, $C4_{Ar}$ -H, ${}^{4}J_{CP}$ = 1.7), 122.96 (d, 1C, $C2_{Ar}$ -Ni, ${}^{2}J_{CP}$ = 35.5), 139.03 (d, 1C, $C3_{Ar}$ -H, $^{3}J_{CP}$ = 3.0), 160.59 (s, 1C, $C5_{Ar}$ -OCH₃), 168.04 (d, 1C, $C1_{Ar}$ -OP, ${}^{2}J_{CP} = 13.4$). ${}^{31}P{}^{1}H{}$ NMR (202.4 MHz, 20 °C, CD₃CN): δ 196.07 (s, 1P). Anal. Calc. for $C_{26}H_{40}O_4P_2Ni_2Br_2$: C, 41.32; H, 5.34. Found: C, 43.41; H, 5.89; N, 0.05.

[(\kappa^{P}, \kappa^{C}-(*i***-Pr)₂PO-(5-Cl-C₆H₃)Ni(***μ***-Br)]₂ (1e). Applying the general procedure given above (at 80 °C for 60 h) gave a dull orange powder. Yield: 542 mg (0.709 mmol, 71%). ¹H NMR (500 MHz, 20 °C, CD₃CN): \delta 1.31 (dd, 6H, CH(CH₃)(CH₃), ³J_{HH} = 7.0, ³J_{HP} = 15.2), 1.46 (dd, 6H, CH(CH₃)(CH₃), ³J_{HH} = 7.2, ³J_{HP} = 17.6), 2.45 (oct, 2H, CH(CH₃)₂, ³J_{HH} \approx ²J_{HP} = 7.2), 6.69 (s, 1H, C6_{Ar}-H), 6.70 (ddd, 1H, C3_{Ar}-H, ³J_{HH} = 8.0, ⁴J_{HP} = 2.1, ⁵J_{HH} = 1.0), 7.12 (dd, 1H, C4_{Ar}-H, ³J_{HH} = 8.0, ⁵J_{HP} = 1.0). ¹³C{¹H} NMR (125.7 MHz, 20 °C, CD₃CN): \delta 16.39 (d, 2C, CH(CH₃)(CH₃), ²J_{CP} = 1.9), 18.00 (d, 2C, CH(CH₃)(CH₃), ²J_{CP} = 2.7), 28.73 (d, 2C, CH(CH₃)(CH₃), ¹J_{CP} = 28.8), 110.44 (d, 1C, C6_{Ar}-H, ³J_{CP} = 13.5), 120.66 (d, 1C, C3_{Ar}-H, ³J_{CP} = 1.6), 131.74 (s, 1C, C6_{Ar}-Cl), 132.09 (d, 1C, C2_{Ar}-Ni, ²J_{CP} = 34.2), 139.43 (d, 1C, C4_{Ar}-H, ⁴J_{CP} = 2.7), 167.35 (d, 1C, C1_{Ar}-OP, ²J_{CP} = 12.8). ³¹P{¹H} NMR (202.4 MHz, 20 °C, CD₃CN): \delta 198.12 (s, 1P). Anal. Calc. for C₂₄H₃₄O₂P₂Cl₂Ni₂Br₂: C, 37.70; H, 4.48. Found: C, 37.38; H, 4.56, N, 0.18.**

 $\label{eq:rescaled} $$ [{\kappa^P, \kappa^C-(i-Pr)_2PO-(3,5-F_2-C_6H_2)}Ni(\mu-Br)]_2$ (1f). Applying the general procedure given above (at 80 °C for 80 h) gave a deep orange $$ (at 80 °C for 80 h) gave a deep orange $$ (begin to the second se$

powder. Yield: 475 mg (0.618 mmol, 62%). ¹H NMR (500 MHz, 20 °C, CD₃CN): δ 1.31 (dd, 6H, CH(CH₃)(CH₃), ${}^{3}J_{HH} = 7.1$, ${}^{3}J_{HP} = 15.4$), 1.48 (dd, 6H, CH(CH₃)(CH₃), ${}^{3}J_{HH} = 7.1$, ${}^{3}J_{HP} = 17.6$), 2.45 (oct, 2H, $CH(CH_3)_2$, ${}^{3}J_{HH} \approx {}^{2}J_{HP} = 7.1$), 6.24 (tdd, 1H, $C4_{Ar}-H$, ${}^{3}J_{HF} = {}^{3}J_{HF'} = 9.9$, ${}^{4}J_{HH} = 2.5, {}^{5}J_{HP} = 1.1), 6.35 \text{ (ddd, 1H, } C6_{Ar}-H, {}^{3}J_{HF} = 9.6, {}^{4}J_{HH} = 2.4, {}^{5}J_{HF}$ = 1.1). ${}^{13}C{}^{1}H{}$ NMR (125.7 MHz, 20 °C, CD₃CN): δ 16.82 (d, 2C, $CH(CH_3)(CH_3)$, ${}^{2}J_{CP} = 2.4$), 18.52 (d, 2C, $CH(CH_3)(CH_3)$, ${}^{2}J_{CP} = 2.2$), 29.58 (d, 2C, CH(CH₃)(CH₃), ${}^{1}J_{CP}$ = 29.8), 95.64 (ddd, 1C, C6_{Ar}-H, ${}^{2}J_{CF}$ = 24.7, ${}^{3}J_{CP} = 13.0$, ${}^{4}J_{CF'} = 3.9$), 97.16 (dd, 1C, $C4_{Ar}$ -H, ${}^{2}J_{CF} = 36.0$, ${}^{2}J_{CF'} =$ 25.0), 112.53 (ddd, 1C, $C2_{Ar}$ -Ni, ${}^{2}J_{CP}$ = 39.4, ${}^{2}J_{CF}$ = 36.2, ${}^{4}J_{CF'}$ = 3.3), 163.13 (dd, 1C, $C3_{Ar}$ -F or $C5_{Ar}$ -F, ${}^{1}J_{CF}$ =240.7, ${}^{3}J_{CF}$ = 15.6), 168.29 (ddd, 1C, $C1_{Ar}$ -OP, ${}^{3}J_{CF}$ = 25.3, ${}^{3}J_{CF'}$ = 14.3, ${}^{2}J_{CP}$ = 10.9), 171.05 (dd, 1C, $C3_{Ar}$ -F or $C5_{Ar}$ -F, ${}^{1}J_{CF}$ = 239.7, ${}^{3}J_{CF}$ = 14.2). ${}^{31}P{}^{1}H$ NMR (202.4 MHz, 20 °C, CD₃CN): δ 193.52 (s, 1P). ¹⁹F NMR (470.4 MHz, 20 °C, CD₃CN): δ -116.38 (q, 1F, $C5_{Ar}$ -F, ${}^{3}J_{HF} \approx {}^{3}J_{H'F} \approx {}^{4}J_{FF} = 9.0$), -92.62 (t, $C3_{Ar}$ -F, ${}^{3}J_{HF} \approx$ ${}^{4}J_{FF}$ = 9.0). Anal. Calc. for C₂₄H₃₂O₂P₂F₄Ni₂Br₂: C, 37.55; H, 4.20. Found: C, 37.75; H, 4.01; N, 0.07.

 $\{(\kappa^{P}, \kappa^{C}-(i-Pr)_{2}PO-(3,5-(MeO)_{2}-C_{6}H_{2})\}$ NiBr(NCMe) (1i-NCMe). The general procedure given above was applied at 70 °C for 16 h gave a dull orange powder. It is important to emphasize that these reaction mixtures were protected from ambient light with aluminum foil during the reaction and during the extraction. Failure to keep out ambient light at all moment, including during work-up, hindered the cyclonickellation reaction. Yield: 480 mg (1.07 mmol, 53%). ¹H NMR (500 MHz, 20 °C, CD₃CN): δ 1.27 (dd, 6H, CH(CH₃)(CH₃), ³J_{HH} = 7.1, ³J_{HP} = 14.9), 1.47 (dd, 6H, CH(CH₃)(CH₃), ³J_{HH} = 7.3, ${}^{3}J_{HP}$ = 17.4), 1.96 (s, 3H, free CH₃CN), 2.38 (oct, 2H, CH(CH₃)₂, ${}^{3}J_{HH} \approx {}^{2}J_{HP} = 7.2$, 3.67 (s, 1H, ArO-CH₃), 3.69 (s, 1H, ArO-CH₃), 5.90 (m, 1H, C4_{Ar}-H), 5.97 (d, 1H, C6_{Ar}-H, ${}^{4}J_{HH}$ = 2.3 Hz). ${}^{13}C{}^{1}H$ NMR (125.7 MHz, 20 °C, CD₃CN): δ 16.60 (d, 2C, CH(CH₃)(CH₃), ²J_{CP} = 2.2), 18.28 (d, 2C, CH(CH₃)(CH₃), ${}^{2}J_{CP} = 2.4$), 29.00 (d, 2C, CH(CH₃)(CH₃), ¹J_{CP} = 29.2), 55.14 (s, 1C, ArO-CH₃), 55.49 (s, 1C, ArO-CH₃), 90.17 (d, 1C, C6_{Ar}-H, J_{CP} = 13.3), 92.58 (s, 1C, C4_{Ar}-H), 107.98 (d, 1C, C2_{Ar}-Ni, ²J_{CP} = 38.4), 161.12 (s, 1C, C5_{Ar}-OMe), 167.24 (d, 1C, C1_{Ar}-OP, ²J_{CP} = 11.3), 168.22 (d, 1C, C3_{Ar}-OMe, ³J_{CP} = 2.0). ³¹P{¹H} NMR (202.4 MHz, 20 °C, CD₃CN): δ 189.97 (s, 1P). Anal. Calc. for C₂₆H₄₀O₂P₂Ni₂Br₂: C, 42.81; H, 5.61; N, 3.12. Found: C, 41.39; H, 5.55; N, 1.69. The lower C- and N-contents of this sample indicate some contamination of the title compound. We have used careful NMR analysis of various samples to rule out the possibility of contamination by the phosphinite adduct 1i-L or the anticipated dimer. On the other hand, we have noted that this compound appears to be lightsensitive, which might explain the presence of impurities; unfortunately, we have not been able to identify the process of the side-products it might generate.

[{κ^P, κ^C-(*i***-Pr)₂PO-(6-Me-C₆H₃)}Ni(μ-Br)]₂ (1j).** Applying the general procedure given above (at 80 °C for 16 h) gave a dull yellowish-orange powder. Yield: 465 mg (0.642 mmol, 64%). ¹H NMR (500 MHz, 20 °C, CD₃CN): δ 1.32 (dd, 6H, CH(CH₃)(CH₃), ³J_{HH} = 7.0, ³J_{HP} = 14.6), 1.35 (dd, 6H, CH(CH₃)(CH₃), ³J_{HH} = 7.2, ³J_{HP} = 17.5), 2.14 (s, 3H, Ar-CH₃), 2.45 (oct, 2H, CH(CH₃), ³J_{HH} \approx ²J_{HP} = 7.1), 6.58 (t, 1H, C4_{Ar}-H, ³J_{HH} = 7.3), 6.82 (d, 1H, C5_{Ar}-H, ³J_{HH} = 7.3), 6.97 (d, 1H, C3_{Ar}-H, ³J_{HH} = 7.6). ¹³C{¹H} NMR (125.7 MHz, 20 °C, CD₃CN): δ 16.05 (m, 2C, CH(CH₃)(CH₃) + Ar-CH₃), 17.79 (d, 2C, CH(CH₃)(CH₃), ²J_{CP} = 2.7), 28.27

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(d, 2C, CH(CH₃)(CH₃), ${}^{1}J_{CP}$ = 29.2), 119.82 (d, 1C, $C6_{Ar}$ -Me, ${}^{4}J_{CP}$ = 12.5), 120.82 (d, 1C, $C4_{Ar}$ -H, ${}^{4}J_{CP}$ = 2.1), 128.01 (s, 1C, $C5_{Ar}$ -H), 132.52 (d, 1C, $C2_{Ar}$ -Ni, ${}^{2}J_{CP}$ = 34.1), 135.80 (d, 1C, $C3_{Ar}$ -H, ${}^{4}J_{CP}$ = 2.5), 165.10 (d, 1C, $C1_{Ar}$ -OP, ${}^{3}J_{CP}$ = 12.1). ${}^{31}P{}^{1}H{}$ NMR (202.4 MHz, 20 °C, CD₃CN): δ 193.78 (s, 1P). Anal. Calc. for $C_{26}H_{40}O_{2}P_{2}Ni_{2}Br_{2}$: C, 43.15; H, 5.57. Found: C, 42.75; H, 5.51; N, 0.06.

 $[\{\kappa^{P}, \kappa^{C} - (i-Pr)_{2}PO - (6-Ph - C_{6}H_{3})\}Ni(\mu - Br)]_{2}$ (1k). Applying the general procedure given above (at 80 °C for 16 h) gave a dull yellowishorange powder. Yield: 625 mg (0.737 mmol, 74%). ¹H NMR (500 MHz, 20 °C, CD₃CN): δ 1.26 (dd, 6H, CH(CH₃)(CH₃), ${}^{3}J_{HH} = 7.3$, ${}^{3}J_{HP} =$ 15.0), 1.48 (dd, 6H, CH(CH₃)(CH₃), ${}^{3}J_{HH}$ = 7.3, ${}^{3}J_{HP}$ = 17.6), 2.41 (oct, 2H, CH(CH₃)₂, ${}^{3}J_{HH} \approx {}^{2}J_{HP} = 7.3$), 6.77 (td, 1H, C4_{Ar}-H, ${}^{3}J_{HH} = 7.6$, ${}^{5}J_{HP} =$ 0.9), 7.06 (dt, 1H, $C3_{Ar}$ -H, $^{3}J_{HH}$ = 7.6, $^{4}J_{HH}$ = $^{4}J_{HP}$ = 1.4), 7.17 (dm, 1H, $C5_{Ar}-H$, ${}^{3}J_{HH} = 7.7$), 7.29 (tt, 1H, $p-C_{Ar}-H$ (Ph), ${}^{3}J_{HH} = 7.3$, ${}^{4}J_{HH} = 1.3$), 7.38 (t, 2H, m-C_{Ar}-H (Ph), ${}^{3}J_{HH}$ = 7.4), 7.49 (dm, 2H, o-C_{Ar}-H (Ph), ${}^{3}J_{HH}$ = 7.3). ${}^{13}C{}^{1}H{}$ NMR (125.7 MHz, 20 °C, CD₃CN): δ 16.98 (d, 2C, $CH(CH_3)(CH_3)$, ${}^{2}J_{CP} = 1.9$, 18.50 (d, 2C, $CH(CH_3)(CH_3)$, ${}^{2}J_{CP} = 2.7$), 29.14 (d, 2C, CH(CH₃)(CH₃), ${}^{1}J_{CP}$ = 29.4), 122.21 (d, 1C, C4_{Ar}-H, ${}^{4}J_{CP}$ = 1.9), 125.16 (d, 1C, $C3_{Ar}$ -H, $^{3}J_{CP}$ = 12.1), 127.99 (d, 2C, m- C_{Ar} -H (Ph), J_{CP} = 139.5), 129.12 (d, 2C, *o*- C_{Ar} -H (Ph), J_{CP} = 106.8), 135.65 (d, 1C, $C2_{Ar}$ -Ni, ${}^{2}J_{CP}$ = 33.0), 138.64 (d, 1C, $C5_{Ar}$ -H, ${}^{5}J_{CP}$ = 2.7), 139.78 (s, 1C, $p-C_{Ar}-H$ (Ph)), 163.78 (d, 1C, $C1_{Ar}-OP$, ${}^{2}J_{CP}$ = 12.6), $C_{qAr}-Ar$ were not detected. ³¹P{¹H} NMR (202.4 MHz, 20 °C, CD₃CN): δ 196.11 (s, 1P). Anal. Calc. for C₃₆H₄₄O₂P₂Ni₂Br₂: C, 51.00; H, 5.23. Found: C, 50.67; H, 5.44; N, 0.05.

 $\{(\kappa^{P}, \kappa^{C}-(i-Pr)_{2}PO-C_{6}H_{4})\}$ NiBr(NCMe) (1a-NCMe). 278 mg (400 µmol) of 1a was suspended in 10 mL Et₂O, and 209 µL MeCN (4.00 mmol, 10 eq) was added. The solid readily dissolved to give a yellow solution which was stirred at room temperature for 30 min. Removal of the solvent under vacuum gave a yellow powder (267 mg, 687 µmol, 86 %). ¹H NMR data in CD₃CN matched the data reported for the dimeric species 1a in CD₃CN (+ 3H for free CH₃CN), and crystallization confirmed the identity of the MeCN adduct.

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- ¹⁴ Complex 1k crystallized in P2₁ space group, but very close to P2₁/a or orthorhombic due to pseudo-symmetry. The nonrestrained refinement process yielded one non-positive definite atom and several atoms featuring ellipsoids with high ratios of atomic displacement parameters. A highly restrained RIGU command was thus applied to all atoms to sort out these issues. It should be noted that data collected at two different temperatures (100 and 150 K) gave very similar results, suggesting that the resolution problems mentioned above are not due to a phase transition at or near the data collection temperature.
- ¹⁵ These values were derived by applying the following equation $\tau 4 = \{360 (\alpha + \beta)\}/141$ wherein α and β are the greater bond angles in the given structure. This approach generates values ranging from 0 for an ideal square plane to 1 for an ideal tetrahedron. For a discussion of this topic see the following reports: (a) Yang, L.; Powell, D. R.; Houser, R. P. *Dalton Trans.* **2007**, 955. (b) Okuniewski, A.; Rosiak, D.; Chojnacki, J.; Becker, B. *Polyhedron* **2015** 90, 47–57.
- ¹⁶ (a) Lefèvre, X.; Spasyuk, D. M.; Zargarian, D. *J. Organomet. Chem.* **2011**, *696*, 864. (b) Lefèvre, X.; Durieux, G.; Lesturgez, S.;
 Zargarian, D. *J. Mol. Catal. A* **2011**, *335*, 1. (c) Lapointe, S.;
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 (d) Salah, A.; Corpet, M.; Khan, N. u-H.; Zargarian, D.; Spasyuk, D. New J. Chem. **2015**, *39*, 6649–6658.
- ¹⁷ This value represents the range of torsion angles in the 4 independent molecules in the unit cell of this compound.
- ¹⁸ Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverría, J.; Cremades, E.; Barragán, F.; Alvarez, C. *Dalton Trans.* **2008**, 2832.
- ¹⁹ We recognize that monomeric acetonitrile adducts likely exchange rapidly with CD₃CN solvent, but we have not attempted to confirm the occurrence of these processes.
- ²⁰ A reviewer of our manuscript suggested that the exchange process in question might occur via an s-trans-to-s-cis isomerization process proceeding via one or the other of the following alternative pathways, a conformational isomerization (square-planar与tetrahedral) or a Ni-Br bond scission followed by rotation around the remaining Ni-µ-Br bond. We have probed these scenarios briefly using DFT studies carried out on the title dimeric complexes. These studies showed that the isolated s-trans dimers are more stable than both the s-cis isomer (by 10.0 kJ/mol) and the proposed tetrahedral intermediate/transition-state (by 68.3 kJ/mol). (See SI for

details.) Thus, the putative s-cis dimer seems feasible, but the proposed conformational isomerization pathway passing through a tetrahedral intermediate/ transition sate seems thermally inaccessible at r.t. We also remain skeptical with respect to an isomerization pathway involving a Ni-Br bond scission, which would generate a 3-coordinate, 14-electron intermediate. Attempts to estimate the energy of such an intermediate by DFT were unsuccessful, implying that it is thermally inaccessible

²¹ Vabre, B.; Spasyuk, D. M.; Zargarian, D. Organometallics **2012**, *31*, 8561–8570.

TOC text for

C–H Nickellation of Phenol-Derived Phosphinites: Regioselectivity and Structures of Cyclonickellated Complexes

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Cyclonickellation of aryl phosphinites derived from substituted phenols is regioselective: high sensitivity to sterics favors nickellation at the less hindered C-H.

Dalton Transactions Accepted Manuscript