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Communication

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Streamlined Preparation and Coordination Chemistry of Hybrid Phosphine−Phosphaalkene Ligands

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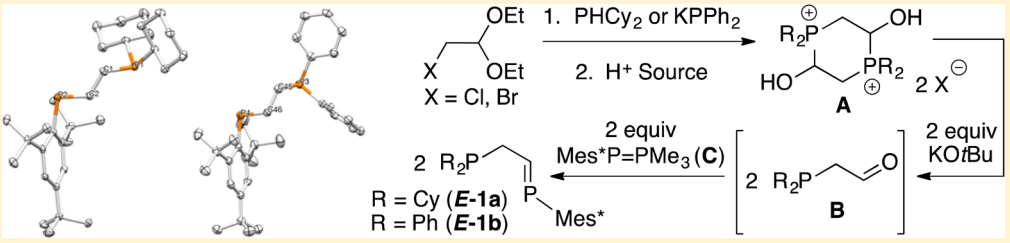
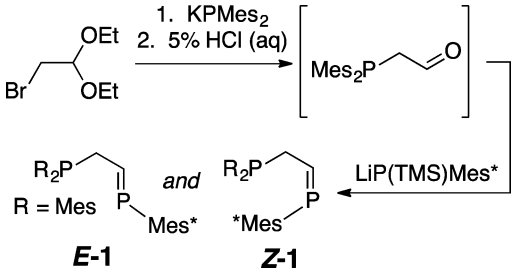
Supporting Information



ABSTRACT: A rationally designed and selective synthesis of hybrid phosphine−phosphaalkene ligands ***E*-1a** ($Cy_2PCH_2CH{=}PMes^*$, Mes* = 2,4,6-tri-*tert*-butylphenyl) and ***E*-1b** ($Ph_2PCH_2CH{=}PMes^*$) was developed using phospha-Wittig methodology. The new hybrid ligands ***E*-1a** and ***E*-1b** were used to prepare the Pd and Pt dichloride complexes $Pd(Cy_2PCH_2CH{=}PMes^*)Cl_2$ (**2a**), $Pd(Ph_2PCH_2CH{=}PMes^*)Cl_2$ (**2b**), $Pt(Cy_2PCH_2CH{=}PMes^*)Cl_2$ (**3a**), and $Pt(Ph_2PCH_2CH{=}PMes^*)Cl_2$ (**3b**). The crystal structures of ***E*-1a**, ***E*-1b**, **2a**·1.33$CHCl_3$, **3a**·CH_3CN, and **3b** were determined. DFT calculations (M06/LACV3P**) on **2a** revealed that the π^* orbital located on the P═C unit is low-lying and accessible. An NBO analysis concluded that the phosphaalkene ligand is a significantly poorer σ donor and a slightly better π acceptor than its tertiary phosphine counterpart, due to the presence of the P═C double bond.

Bidentate phosphines are typically designed based on a 2-fold axis of proper rotation (C_2).[1] However, hybrid ligands,[2] in which two sterically and electronically different phosphorus groups are linked, represent an underutilized but valuable class of ligands.[3] Mixed phosphine−phosphinidines[4,5] (phosphaalkenes)[6] were targeted as potential supporting ligands for Pd-catalyzed polymerization and oligomerization of ethylene.[4] However, synthesis of **1** as a mixture of phosphaalkene isomers (*E* or *Z*) in a 10:3 ratio, with a 17% isolated yield of the major isomer (Scheme 1: R = Mes = 2,4,6-trimethylphenyl; Mes* = 2,4,6-tri-*tert*-butylphenyl)[7] was plagued by "instability of the ligand and synthetic intermediates (high air and moisture sensitivity, low crystallinity)".[4,8]

Scheme 1. Literature Synthesis of Hybrid Ligands 1[4]



Perhaps overlooked due to synthetic difficulties,[9] development of two carbon-bridged hybrid ligands, incorporating a modular and tunable phosphine group[10] and a π-accepting phosphaalkene[11] unit, could find application in catalytic and bond activation processes.[7,12] Bidentate (bis)phosphaalkene ligands[13] have been used in hydroamination,[7] hydrosilylation,[14] conjugate addition,[15] and other transition-metal-catalyzed reactions.[16] Redox-active/noninnocent[17] phosphaalkene-based pincer complexes have been implicated in N−H,[18] C−H,[19] and P−C bond cleavage events,[20] catalytic N-alkylation of amines with alcohols,[21] unanticipated disproportionations[22] and reductions,[23] and the stabilization of low-coordinate electron-rich metal complexes.[24] The range of applications is consistently tied to the accessibility and responsiveness of the low-lying π^* orbital located on the P═C fragment.[11,13] This reactivity enhancement with redox-active/noninnocent ligands,[17] combined with the opportunity to add diversity[25] to an underexplored ligand pool, provided the impetus required to reinvest in a modified synthesis of ligands of type **1**.

Reexamination of the synthetic pathway to **1** suggested that trapping the first phosphinated intermediate as an air-stable phosphonium dimer[26] would simplify the reaction. Controlled

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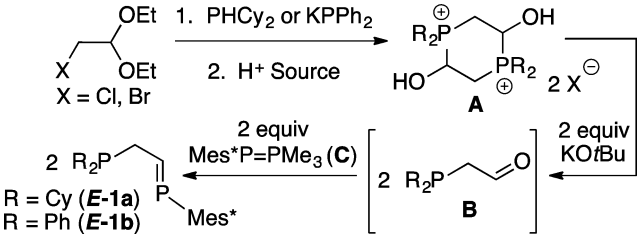
fragmentation of the dimer with base to release the tethered aldehyde[27] would allow treatment with phospha-Wittig[28] reagents (Mes*P═PMe$_3$) to access hybrid phosphine−phosphaalkene ligands in an *E*-selective fashion. Here we report the successful implementation of this strategy and the coordination chemistry of these new ligands with Pd(II) and Pt(II).

Phosphination of the functionalized acetals with PHCy$_2$ or KPPh$_2$ affords phosphonium dimers (**A**: R = Cy, X = Br; R = Ph, X = Cl) as described in the literature (Scheme 2).[26]

Scheme 2. Selective Synthesis of *E*-1a and *E*-1b



Treatment of **A**[26] with KO*t*Bu (2 equiv in toluene) generated the phosphine-functionalized aldehyde **B**,[27] which reacted with the phosphinidene transfer agent Mes*P═PMe$_3$ (**C**)[29] to give selective formation of ***E*-1a** and ***E*-1b**,[30] characterized by the expected two doublets (***E*-1a**, J_{PP} = 37 Hz; ***E*-1b**, J_{PP} = 47 Hz) in their $^{31}P\{^1H\}$ NMR spectra.

E*-1a** and ***E*-1b** were isolated as pale yellow solids and characterized by $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR spectroscopy, mass spectrometry, and elemental analysis. The ^1H NMR signals of the CH$_2$ protons located on the two-carbon backbone are particularly diagnostic, appearing as doublets of doublets of doublets (E*-1a**, J = 2.5, 9.5, 22 Hz; ***E*-1b**, J = 2.5, 9, 21 Hz). Although partially hidden under the prominent Mes* resonance, the phosphaalkene proton of ***E*-1a** displayed a complex doublet of triplets of doublets pattern; the analogous signal in ***E*-1b** was buried beneath the PPh$_2$/Mes* region.[30] The structures of ***E*-1a** and ***E*-1b** were confirmed by X-ray crystallography (Figure 1).

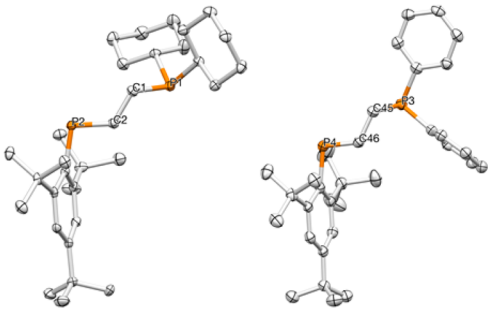
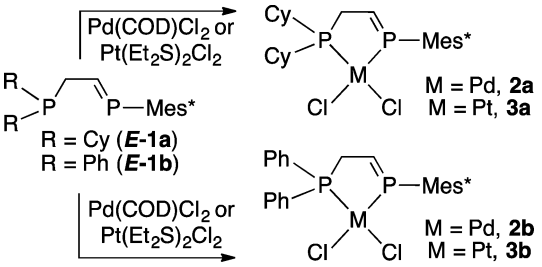


Figure 1. X-ray crystal structures of ***E*-1a** (left) and ***E*-1b** (right). Selected bond lengths (Å): for ***E*-1a**, P_1-C_1 = 1.8685(16), P_2-C_2 (P═C) = 1.6645(17); for one of the two independent molecules of ***E*-1b**, P_3-C_{45} 1.867(2), P_4-C_{46} (P═C) = 1.663(2).

Addition of ***E*-1a** in chloroform to Pd(COD)Cl$_2$ or Pt(Et$_2$S)$_2$Cl$_2$ generated dichlorides **2a** and **3a**, respectively (Scheme 3). The $^{31}P\{^1H\}$ NMR spectra of both complexes showed a dramatic upfield chemical shift change versus the free ligand with greatly reduced J_{PP} couplings (**2a**, J_{PP} = 17 Hz; **3a**, J_{PP} = 3 Hz), with **3a** also displaying Pt satellites (J_{PtP} = 4520 Hz, P═C; J_{PtP} = 3280 Hz, PCy$_2$).

Scheme 3. Synthesis of Pd(II) and Pt(II) Complexes



Likewise, ***E*-1b** generated **2b** and **3b** (J_{PtP} = 4425 Hz, P═C; J_{PtP} = 3390 Hz, PPh$_2$). The significantly larger J_{PtP} couplings of the phosphaalkenes are consistent with higher s character in the P donor orbital (vide infra). Complexes **2** and **3** were fully characterized by $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR spectroscopy, mass spectrometry, and elemental analysis. In both sets of metal complexes, the ^1H NMR spectra displayed a distinctive doublet of doublets of triplets signal for the phosphaalkene proton.[30] Structures of **2a** and **3a**,**b** were unequivocally established by X-ray crystallography (Figure 2), exhibiting distorted-square-planar geometries around the Pd/Pt center, with the hybrid ligands adopting bite angles of less than 86°.[31]

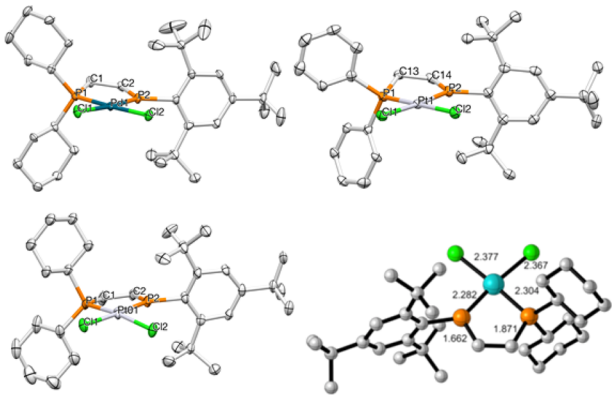


Figure 2. X-ray crystal structures of **2a** (top left), **3a** (bottom left), and **3b** (top right). Selected bond lengths (Å): for **2a**, Pd−P_1 = 2.2558(13), Pd−P_2 = 2.2194(14), P_1-C_1 = 1.863(5), P_2-C_2 (P═C) = 1.648(5), Pd−Cl_1 = 2.3485(13), Pd−Cl_2 = 2.3748(13); for **3a**, P_1-C_1 = 1.847(8), P_2-C_2 (P═C) = 1.651(8); for **3b**, P_1-C_{13} = 1.850(9), P_2-C_{14} (P═C) = 1.653(9). The DFT calculated structure of **2a** is shown at the bottom right with selected bond lengths (Å).

The significant upfield shifts in the ^{31}P NMR spectra on coordination are not correlated with changes in the P═C bond length, which does not increase upon binding to Pd or Pt centers, an initially surprising observation given the reported π-accepting ability of phosphaalkenes.[11,18,20−23] However, phosphaalkene-derived pincers and bidentate ligands[32,33] also showed negligible change in the P═C bond length upon coordination to Pd(II) or Pt(II), and the π^* orbitals located on these phosphaalkene-supported complexes were readily able to reversibly accept an electron[32] or undergo nucleophilic attack.[33] Furthermore, a recent report on Ir PNP pincers featuring phosphaalkene donor groups[19] suggested that the degree of change in the P═C bond length and upfield shift of the ^{31}P NMR signal is governed by both the electron-donating ability

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of the X-type ligand and the overall charge on the metal complex.[34] Alternatively, the substantial increase in the C═P−C angle (~10°) on coordination may reflect increased s character in the P−C bonds, leaving the P═C bond length largely unperturbed.

DFT studies (M06/LACV3P**++) were carried out on the full molecules **2a** and the free ligand ***E*-1a**. Full details are provided in the Supporting Information.[30] The calculated structure for **2a** (Figure 2) shows an excellent match with the crystallographic metrics, including a slightly shorter bond from Pd to the phosphaalkene in comparison to the phosphine and a slightly shorter Pd−Cl bond trans to the phosphaalkene. Two minima were located for ***E*-1a**: a gauche conformer similar to that found crystallographically, and a cis conformer with a P−C−C−P dihedral angle of 1° lying only 3.1 kcal/mol higher in energy. Clearly, the energy cost of ligand distortion for cis chelation is small. For energy comparisons, we have utilized data for the cis conformer of ***E*-1a** and its cis-chelated complex **2a**.

In *cis*-***E*-1a**, the C═P π/π^* energy gap is 5.52 eV. Coordination to Pd in **2a** stabilizes both π and π^* levels slightly with a small increase in the π/π^* gap to 5.62 eV. A partial MO energy level diagram for **2a** is shown in Figure 3.

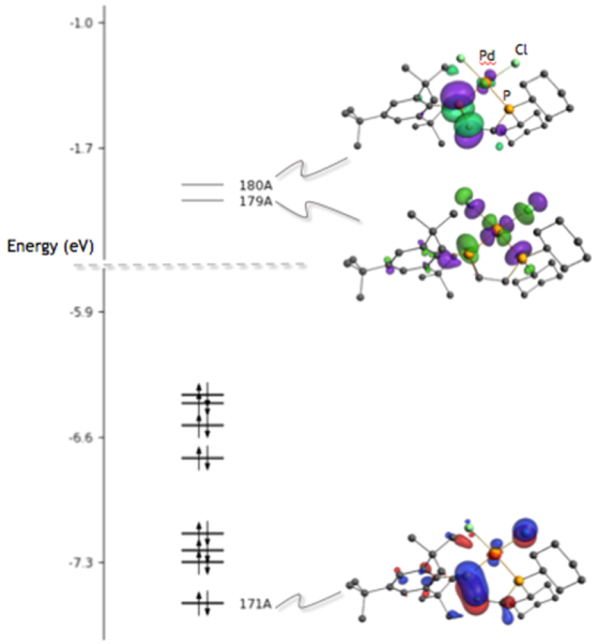


Figure 3. Partial MO energy level diagram for **2a**.

The C═P π MO is HOMO-7 (171A); the higher occupied MOs are Pd and Cl lone pair combinations. The C═P π^* MO (180A) lies slightly above the LUMO (179A), the expected Pd−ligand σ^* combination. The C═P π^* orbital remains available energetically and provides opportunities for further ligand functionalization via nucleophilic attack or reduction.

Donor/acceptor capabilities of the two phosphorus centers were evaluated using the natural bond orbital (NBO) method,[35] with a reference Lewis structure[36] chosen (using the $CHOOSE keyword in NBO) as the ***E*-1a** ligand and the bent $PdCl_2$ fragments frozen in their geometries in **2a**. Relative to this reference, delocalization results in donor NBOs showing depletion from full occupancies of 2 and acceptor NBOs showing occupancies above 0. Second-order perturbation analysis of the Fock matrix provides energy stabilizations resulting from individual donor/acceptor delocalizations, which are visualized as natural localized molecular orbitals (NLMOs). Key data are provided in Figure 4.

The two phosphorus lone pairs are distinguished by significantly different hybridizations: P(2) $sp^{2.50}$ and P(3) $sp^{1.55}$. As a result, despite its slightly longer bond length to Pd, P(2) is the better σ donor to $PdCl_2$. The occupancy of the P(2) lone pair (1.30) is depleted more than that of P(3) (1.54), and

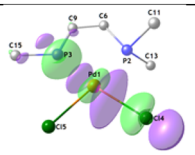
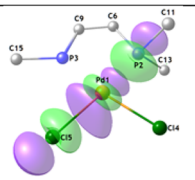
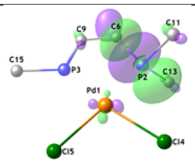
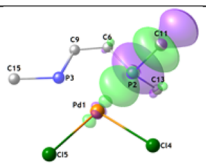
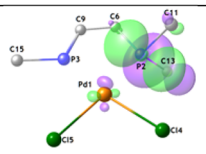
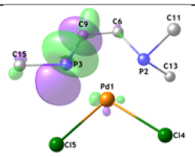
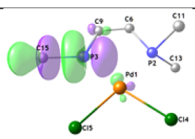
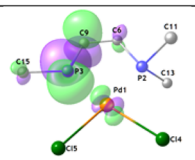
NLMO	Donor/acceptor delocalization; acceptor NBO occupancy	Stabilization Energy (kcal/mol)
	P(3)lp→Pd-Cl(4) σ* Pd-Cl(4) σ* 0.57	E = 139.6
	P(2)lp→Pd-Cl(5) σ* Pd-Cl(5) σ* 0.61	E = 213.1
	Pd(d)→P(2)-C(6) σ* P(2)-C(6) σ* 0.13 in plane	E = 2.2
	Pd(d)→P(2)-C(11) σ* P(2)-C(11) σ* 0.06 out of plane	E = 2.0
	Pd(d)→P(2)-C(13) σ* P(2)-C(13) σ* 0.07 out of plane	E = 1.5
	Pd(d)→P(3)-C(9) σ* P(3)-C(9) σ* 0.05 in plane	E = 1.4
	Pd(d)→P(3)-C(15) σ* P(3)-C(15) σ* 0.04 in plane	E = 2.7
	Pd(d)→P(3)-C(9) π* P(3)-C(9) π* 0.13 out of plane	E = 7.4

Figure 4. Calculated NLMOs with NBO occupancies and delocalization energies for the interactions of ligand ***E*-1a** with $PdCl_2$ in complex **2a**. For clarity only those carbon atoms directly bound to phosphorus are shown.

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increased occupancies of Pd−Cl(4) σ^* (0.61) in comparison to Pd−Cl(5) σ^* (0.57) are consistent with a slightly shorter Pd−Cl bond trans to the phosphaalkene. Stabilization energies corresponding to these delocalizations are 213.1 and 139.6 kcal/mol, respectively. Unsurprisingly, the π interactions are much smaller. The π-acceptor components for the tertiary phosphorus P(2) are the three P−C σ^* orbitals; of these P−C(6) lies in the coordination plane and P−C(11) and P−C(13) lie out of the plane. The in-plane energy stabilization for P(2) is 2.2, and the two out of plane interactions sum to 3.5, giving a total of 5.7 kcal/mol in π-acceptor interactions. In contrast, P(3) has two in-plane interactions involving P−C σ^* orbitals affording 4.1 kcal/mol stabilization, and a significant out-of-plane interaction with the P═C π^* orbital (7.4 kcal/mol) giving a total 11.5 kcal/mol stabilization. This method of appraisal concludes that the phosphaalkene component is a poorer σ donor and a slightly better π acceptor than its tertiary phosphine partner.

In summary, we have reported a rationally designed and streamlined synthesis of an unexplored class of hybrid phosphine−phosphaalkene ligands. The methodology is modular and tunable, as phosphine groups featuring either large alkyl groups (***E*-1a**) or small aryl groups (***E*-1b**) were both tolerated. Furthermore, the coordination chemistry with Pd and Pt to afford **2a**,**b** and **3a**,**b** was straightforward, yielding robust and crystalline metal−ligand platforms. Future investigations will target synthesizing an expanded library of new hybrid ligands, with the goal of exploiting the innate reactivity of the P═C bond to enhance catalytic reactions and bond activation events. The low-lying π^* component of the P═C bond suggests these hybrid phosphine−phosphaalkene ligands may harness redox-active/noninnocent behavior,[37] which will be the focus of upcoming reactivity studies.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00101.

Experimental details, NMR spectra, and full details of DFT and NBO computational methodology (PDF)
Crystallographic data (CIF)
Crystallographic data (CIF)
Crystallographic data (CIF)
Crystallographic data (CIF)
Crystallographic data (CIF)
Cartesian coordinates (XYZ)
Cartesian coordinates (XYZ)
Cartesian coordinates (XYZ)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Whitesell, J. K. *Chem. Rev.* **1989**, *89*, 1581−1590. (b) Burk, M. J. *Acc. Chem. Res.* **2000**, *33*, 363−372.
(2) (a) Czauderna, C. F.; Cordes, D. B.; Slawin, A. M. Z.; Müller, C.; van der Vlugt, J. I.; Vogt, D.; Kamer, P. C. J. *Eur. J. Inorg. Chem.* **2014**, *2014*, 1797−1810. (b) Ohashi, A.; Kikuchi, S.; Yasutake, M.; Imamoto, T. *Eur. J. Org. Chem.* **2002**, *2002*, 2535−2546.
(3) (a) Hoge, G.; Wu, H.-P.; Kissel, W. S.; Pflum, D. A.; Greene, D. J.; Bao, J. *J. Am. Chem. Soc.* **2004**, *126*, 5966−5967. (b) Gridnev, I. D.; Imamoto, T.; Hoge, G.; Kouchi, M.; Takahashi, H. *J. Am. Chem. Soc.* **2008**, *130*, 2560−2572. (c) Noonan, G. M.; Fuentes, J. A.; Cobley, C. J.; Clarke, M. L. *Angew. Chem., Int. Ed.* **2012**, *51*, 2477−2480.
(4) Daugulis, O.; Brookhart, M.; White, P. S. *Organometallics* **2002**, *21*, 5935−5943.
(5) Aktas, H.; Slootweg, J. C.; Lammertsma, K. *Angew. Chem., Int. Ed.* **2010**, *49*, 2102−2113.
(6) The nomenclature used in ref 4 is somewhat misleading. Formally, phosphinidenes are phosphorus analogues of carbenes and nitrenes. Phosphaalkanes are the phosphorus versions of alkenes. The ligands in ref 4 are phosphaalkenes.
(7) Takita, R.; Takada, Y.; Jensen, R. S.; Okazaki, M.; Ozawa, F. *Organometallics* **2008**, *27*, 6279−6285.
(8) Brookhart, M.; Daugulis, O. WO 03/076450A1, 2003.
(9) Kyba, E. P.; Kerby, M. C.; Rines, S. P. *Organometallics* **1986**, *5*, 1189−1194.
(10) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313−346.
(11) Le Floch, P. *Coord. Chem. Rev.* **2006**, *250*, 627−681.
(12) (a) Brauer, D. J.; Liek, C.; Stelzer, O. *J. Organomet. Chem.* **2001**, *626*, 106−112. (b) Liang, H.; Nishide, K.; Ito, S.; Yoshifuji, M. *Tetrahedron Lett.* **2003**, *44*, 8297−8300.
(13) Ozawa, F.; Yoshifuji, M. *Dalton Trans.* **2006**, 4987−4995.
(14) Hayashi, A.; Yoshitomi, T.; Umeda, K.; Okazaki, M.; Ozawa, F. *Organometallics* **2008**, *27*, 2321−2327.
(15) Jensen, R. S.; Umeda, K.; Okazaki, M.; Ozawa, F.; Yoshifuji, M. *J. Organomet. Chem.* **2007**, *692*, 286−294.
(16) (a) Ito, S.; Nanko, M.; Mikami, K. *ChemCatChem* **2014**, *6*, 2292−2297. (b) Dugal-Tessier, J.; Dake, G. R.; Gates, D. P. *Org. Lett.* **2010**, *12*, 4667−4669.
(17) Chirik, P. J. *Inorg. Chem.* **2011**, *50*, 9737−9740.
(18) (a) Chang, Y.-H.; Nakajima, Y.; Tanaka, H.; Yoshizawa, K.; Ozawa, F. *J. Am. Chem. Soc.* **2013**, *135*, 11791−11794. (b) Chang, Y.-H.; Nakajima, Y.; Tanaka, H.; Yoshizawa, K.; Ozawa, F. *Organometallics* **2014**, *33*, 715−721.
(19) Chang, Y.-H.; Takeuchi, K.; Wakioka, M.; Ozawa, F. *Organometallics* **2015**, *34*, 1957−1962.
(20) Lin, Y.-F.; Nakajima, Y.; Ozawa, F. *Dalton Trans.* **2014**, *43*, 9032−9037.
(21) (a) Nakajima, Y.; Okamoto, Y.; Chang, Y.-H.; Ozawa, F. *Organometallics* **2013**, *32*, 2918−2925. (b) Chang, Y.-H.; Nakajima, Y.; Ozawa, F. *Organometallics* **2013**, *32*, 2210−2215.
(22) Lin, Y.-F.; Ichihara, N.; Nakajima, Y.; Ozawa, F. *Organometallics* **2014**, *33*, 6700−6703.
(23) Nakajima, Y.; Ozawa, F. *Organometallics* **2012**, *31*, 2009−2015.
(24) (a) Nakajima, Y.; Shiraishi, Y.; Tsuchimoto, T.; Ozawa, F. *Chem. Commun.* **2011**, *47*, 6332−6334. (b) Nakajima, Y.; Nakao, Y.; Sakaki, S.; Tamada, Y.; Ono, T.; Ozawa, F. *J. Am. Chem. Soc.* **2010**, *132*, 9934−9936.
(25) Lennon, I. C.; Pilkington, C. J. *Synthesis* **2003**, *2003*, 1639−1642.
(26) (a) Mikhailine, A. A.; Kim, E.; Dingels, C.; Lough, A. J.; Morris, R. H. *Inorg. Chem.* **2008**, *47*, 6587−6589. (b) Lagaditis, P. O.; Mikhailine, A. A.; Lough, A. J.; Morris, R. H. *Inorg. Chem.* **2010**, *49*,

DOI: 10.1021/acs.organomet.6b00101
Organometallics XXXX, XXX, XXX−XXX

1094−1102. (c) Zuo, W.; Morris, R. H. *Nat. Protoc.* **2015**, *10*, 241−257.
(27) Matt, D.; Ziessel, R.; de Cian, A.; Fischer, J. *New J. Chem.* **1996**, *20*, 1257−1263.
(28) (a) Shah, S.; Protasiewicz, J. D. *Chem. Commun.* **1998**, 1585−1586. (b) Shah, S.; Protasiewicz, J. D. *Coord. Chem. Rev.* **2000**, *210*, 181−201.
(29) Deschamps, E.; Deschamps, B.; Dormieux, J. L.; Ricard, L.; Mézailles, N.; Le Floch, P. *Dalton Trans.* **2006**, 594−602.
(30) See the Supporting Information for experimental details, selected NMR spectra, DFT calculations, and X-ray crystallography data.
(31) Birkholz, M.-N.; Freixa, Z.; van Leeuwen, P. W. N. M. *Chem. Soc. Rev.* **2009**, *38*, 1099−1118.
(32) Jouaiti, A.; Geoffroy, M.; Terron, G.; Bernardinelli, G. *J. Am. Chem. Soc.* **1995**, *117*, 2251−2258.
(33) (a) Jouaiti, A.; Geoffroy, M.; Bernardinelli, G. *Chem. Commun.* **1996**, 437−438. (b) Jouaiti, A.; Geoffroy, M.; Terron, G.; Bernardinelli, G. *J. Chem. Soc., Chem. Commun.* **1992**, 155−156.
(34) Related rationalizations are well established in metal carbonyl chemistry (see ref 10).
(35) (a) Glendening, E. D.; Landis, C. R.; Weinhold, F. *Wiley Interdisciplinary Reviews: Computational Molecular Science* **2012**, *2*, 1−42. (b) Weinhold, F.; Landis, C. R. *Discovering Chemistry with Natural Bond Orbitals*; Wiley: Hoboken, NJ, 2012. (c) Weinhold, F.; Landis, C. R. *Valency and Bonding: A Natural Bond Orbital Donor-Acceptor Perspective*; Cambridge University Press: Cambridge, U.K., 2005.
(36) The importance of a judicious choice of reference structure is discussed in: Landis, C. R.; Hughes, R. P.; Weinhold, F. *Organometallics* **2015**, *34*, 3442−3449.
(37) (a) Chirik, P. J.; Wieghardt, K. *Science* **2010**, *327*, 794−795. (b) Serin, S. C.; Patrick, B. O.; Dake, G. R.; Gates, D. P. *Organometallics* **2014**, *33*, 7215−7222.

DOI: 10.1021/acs.organomet.6b00101
Organometallics XXXX, XXX, XXX−XXX