## **ORGANOMETALLICS**

# Electronic Properties of a Cationic Triphenylphosphine Ligand Decorated with a $(\eta^5-C_5H_5)$ Fe Group in Late-Transition-Metal Complexes

Christian Malchau, Florian Loose, Yannick Mees, Jens Duppe, Yu Sun, Gereon Niedner-Schatteburg, and Werner R. Thiel\*



iron(II) hexafluorophosphate (1) are reported. Complexes of ligand 1 with the late transition metals ruthenium, osmium, rhodium, and iridium as well as palladium and platinum were isolated in generally good yields, and the solid-state structures of most of them were determined. On the basis of the <sup>195</sup>Pt-<sup>31</sup>P NMR coupling constant measured for *trans*-(1)<sub>2</sub>PtCl<sub>2</sub> and the carbonyl absorption band in the IR spectrum of *trans*-(1)<sub>2</sub>Rh(CO)Cl, the electronic influence of the ligand on the metal center was evaluated. These measurements are supported by density functional theory (DFT) calculations, performed on the corresponding tricarbonylnickel(0) complex in order to determine the Tolman electronic parameter (TEP) of ligand 1.

#### ■ INTRODUCTION

In homogeneous catalysis, phosphines are among the most frequently used ligands.<sup>1</sup> They impart good solubility of catalysts in organic solvents and have in particular the ability to stabilize metal centers in lower oxidation states that are of importance in many catalytic cycles. A further advantage is the great variability of phosphines. This enables tailoring such ligands in order to rationally optimize the reactivity and selectivity of metal-centered catalysts. The Tolman steric parameter (TSP) and the Tolman electronic parameter (TEP), for example, allow the steric and electronic properties of phosphine ligands to be evaluated.<sup>2</sup> Although there are numerous anionic or neutral phosphines with different  $\sigma$ donating properties, only a few ligands of this type with  $\pi$ acceptor character have been reported so far.<sup>3</sup> Enhanced acceptor properties can be realized by the introduction of a positive charge or by strongly electron withdrawing substituents in close proximity to the phosphorus donor site. Other typical examples are phosphorus compounds with heteroatoms directly bonded to the phosphorus atom and therefore energetically low lying  $\pi$ -acceptor orbitals such as PF<sub>3</sub>, and phosphites. Phosphites are widely used as ligands in catalysis.<sup>4</sup> In contrast, phosphorus species with directly bound halogens are highly toxic and air-sensitive and thus have been reported only rarely as ligands in transition-metal chemistry. Alternatively, phosphines having perfluoroalkyl and -aryl substituents have found application as less-donating and

more-accepting ligands.<sup>3c,6</sup> An entirely different approach sets the focus on positively charged phosphine ligands in order to generate comparably strong  $\pi$ -accepting properties. Synthesis strategies to access such compounds include the reaction of chloro(dialkyl)- or chloro(diaryl)phosphines with Lewis bases, imidazolium carboxylates, or 2-silylimidazolium salts.<sup>3a,d,7</sup> During the last few years, Alcarazo et al. in particular developed additional methods starting from secondary phosphines.<sup>3a,d,e,8</sup> Cationic phosphines have recently found application in palladium-catalyzed cross-coupling reactions, hydroformylation, hydrosilylation, hydroarylation, and cycloisomerization, to name just a few examples.<sup>3e,9</sup> In addition, their use in phase-transfer catalysis and in the elucidation of reaction mechanisms by means of electrospray ionization mass spectrometry has been documented.<sup>3a,e</sup>

In 2016 we reported an improved synthesis of the ligand ( $\eta^{5}$ -cyclopentadienyl)( $\eta^{6}$ -diphenylphosphinobenzene)iron(II) hexafluorophosphate (1), which was first reported by Roberts et al. in 1995.<sup>10</sup> Herein ferrocene is first reacted with

Received: June 16, 2020

chlorobenzene in a ligand exchange reaction to give  $(\eta^{6} - \text{chlorobenzene})(\eta^{5} - \text{cyclopentadienyl})\text{iron(II})$  hexafluorophosphate (Scheme 1).<sup>11</sup> The product is then treated with lithium

#### Scheme 1. Synthesis of the Cationic Phosphine Ligand $1^a$



"Legend: (i) C<sub>6</sub>H<sub>5</sub>Cl, AlCl<sub>3</sub>, NH<sub>4</sub>PF<sub>6</sub>, reflux, 4 h; (ii) LiPPh<sub>2</sub>, thf, 18 h, rt.

diphenylphosphide to obtain the cationic phosphine ligand in a nucleophilic aromatic substitution reaction. Furthermore, we were able to synthesize the first heterobimetallic complex with gold(I) chloride based on this cationic phosphine ligand.

In a continuation of this work, we now report on the synthesis and characterization of further cationic transitionmetal complexes with ligand 1 as well as on a detailed investigation of its electronic properties.

#### RESULTS AND DISCUSSION

**Complex Synthesis.** Our attention was first directed to ruthenium and osmium, the heavy homologues of iron. The diamagnetic compounds  $[(\eta^6-p\text{-}cymene)\text{MCl}_2]_2$  (M = Ru, Os) seemed to be suitable precursors.<sup>12</sup> They both are known to react readily with phosphines to yield complexes of the type  $(\eta^6-p\text{-}cymene)\text{MCl}_2(L)$  (L = phosphine ligand).<sup>12b,13</sup> Treatment of 1/2 equiv of the dimers  $[(\eta^6-p\text{-}cymene)\text{MCl}_2]_2$  with phosphine 1 gave the corresponding cationic phosphine complexes 2 and 3 in yields of 90 and 70%, respectively (Scheme 2).

Scheme 2. Synthesis of the Ruthenium(II) and Osmium(II) Complexes 2 and  $3^a$ 



<sup>*a*</sup>Legend: (i)  $[(\eta^6\text{-}p\text{-}cymene)MCl_2]_2$ , CH<sub>2</sub>Cl<sub>2</sub>, rt, 16 h.

The first evidence for the successful synthesis of compounds 2 and 3 was obtained by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy. The <sup>31</sup>P spectra of 2 and 3 showed in addition to the typical septet resonance of the hexafluorophosphate anion at -144.6 ppm the resonance of the phosphine donor at +27.5 (2, M = Ru) and -15.6 ppm (3, M = Os), respectively.

In comparison to the free ligand 1 (singlet at -5.9 ppm) with a signal in the same range as for PPh<sub>3</sub> (-6.0 ppm), <sup>14</sup> the resonance for the ruthenium complex 2 is shifted to lower field, while coordination to an osmium center in 3 induces a high-field shift. Similar data have been reported in the literature for ( $\eta^{6}$ -*p*-cymene)RuCl<sub>2</sub>(PPh<sub>3</sub>).<sup>13</sup> The rather pronounced shift of the phosphine resonance to higher field observed for the third-row transition metal osmium is in good agreement with the shift for the corresponding triphenylphosphine complex ( $\eta^{6}$ -*p*-cymene)OsCl<sub>2</sub>(PPh<sub>3</sub>) ( $\delta$  -13.2 ppm). In the <sup>1</sup>H NMR spectra

of 2 and 3 the resonances of all protons were assigned unambiguously. The signal of the cyclopentadienyl protons appears at about +4.4 ppm. The resonances of the protons at the  $\eta^6$ -coordinating cymene ring are observed as two doublets at about 5.5 ppm. In comparison to this, the <sup>1</sup>H NMR resonances of the  $\eta^6$ -coordinating phenyl ring are shifted to lower field (about +6.2 and +6.9 ppm, respectively) due to the positively charged CpFe group that is coordinated to this fragment. Further resonances in the aromatic region are assigned to the two phenyl groups. Three signals in the aliphatic region are allocated to the methyl and the isopropyl substituents of the cymene ring. In addition to the NMR spectra, elemental analysis and ESI mass spectrometry further support the structural identification. ESI mass spectrometry shows the expected signals of the cations  $2^+$  and  $3^+$  without any fragmentation and with matching isotope patterns.

Single crystals of the ruthenium(II) complex 2, suitable for a X-ray diffraction study, were obtained by slow diffusion of diethyl ether into a saturated solution of 2 in dichloromethane. Figure 1 shows the molecular structure of 2 and summarizes typical bond parameters.



Figure 1. Molecular structure of compound 2 in the solid state. Characteristic bond lengths (Å) and angles (deg): Fe1–Cp 1.6658(5), Fe1–Ar 1.5390(5), Ru1–Cl1 2.4080(9), Ru1–Cl2 2.4221(9), Ru1–P1 2.3589(9), Ru1–Ar 1.7074(3), Cp–Fe1–Ar 177.45(4), Cl1–Ru1–Cl2 88.96(3), Cl1–Ru1–P1 88.17(3), Cl1–Ru1–Ar 124.44(2), Cl2–Ru1–P1 87.02(3), Cl2–Ru1–Ar 126.90(3), P1–Ru1–Ar 128.56(3). Cp denotes the center of the  $\eta^5$ -coordinated cyclopentadienyl ring. Ar denotes the centers of the  $\eta^6$ -coordinated arene rings.

While the distances between Fe1 and the carbon atoms of the  $\eta^5$ -coordinated cyclopentadienyl ring (average 2.051 Å) are slightly shorter than the distances between Fe1 and the carbon atoms of the  $\eta^6$ -coordinated phenyl ring (average 2.088 Å), the distances to the corresponding ring centers behave in the opposite way, due to the different ring sizes. According to the ionic radii of iron(II) and ruthenium(II) the Ru1–Ar distance is about 0.16 Å longer than the Fe1–Ar distance. The Ru1–P1 distance is slightly elongated in comparison to that in the corresponding ruthenium(II) complex ( $\eta^6$ -*p*-cymene)-RuCl<sub>2</sub>(PPh<sub>3</sub>) (2.3438(6) Å), bearing a triphenylphosphine ligand.<sup>15</sup> This might be interpreted as a result of a reduced  $\sigma$ -donor ability due to the positively charged phosphine ligand.

Treatment of 1/2 equiv of the dimeric rhodium(I) complex  $[(CO)_2 Rh(\mu_2 - Cl)]_2^{16}$  with ligand 1 resulted in the formation of the dicationic complex 4 in almost quantitative yield (Scheme 3).

Herein, two phosphines, one carbonyl, and one chlorido ligand complete the square-planar coordination sphere at the rhodium center. The  ${}^{1}H$  NMR spectrum of compound 4

Scheme 3. Synthesis of the Rhodium(I) Complex  $4^{a}$ 



<sup>*a*</sup>Legend: (i)  $[(CO)_2 Rh(\mu_2 - Cl)]_2$ , CH<sub>2</sub>Cl<sub>2</sub>, rt, 16 h.

essentially resembles the spectra of 2 and 3. Generally the resonances are slightly shifted to lower field. The resonance of the cyclopentadienyl ring is found at +5.03 ppm, while this resonance appears at about +4.4 ppm in the <sup>1</sup>H NMR spectra of 2 and 3. We assign this to the increased positive charge. The <sup>31</sup>P NMR spectrum shows a doublet at +26.9 ppm with a <sup>1</sup>J<sub>RhP</sub> coupling constant of 131.0 Hz. Both values are close to the data reported for CO(Cl)Rh(PPh<sub>3</sub>)<sub>2</sub> (+30.0 ppm, <sup>1</sup>J<sub>RhP</sub> = 127 Hz).<sup>17</sup>

Suitable single crystals for an X-ray structure analysis were obtained by recrystallization of 4 by slow diffusion of diethyl ether into a solution in acetonitrile. Figure 2 shows the molecular structure of 4 and summarizes typical bond parameters.



**Figure 2.** Molecular structure of compound 4 in the solid state. Characteristic bond lengths (Å) and angles (deg): Fe1–Cp 1.6719(8), Fe1–Ar 1.5350(8), Fe2–Cp 1.6699(8), Fe2–Ar 1.5315(7), Rh1–Cl1 2.3651(12), Rh1–P1 2.3331(11), Rh1–P2 2.3265(11), Rh1–C47 1.812(5), O1–C47 1.155(7), Cp–Fe1–Ar 177.15(6), Cp–Fe2–Ar 177.64(6), Cl1–Rh1–P1 91.53(4), Cl1–Rh1–P2 91.29(4), Cl1–Rh1–C47 175.66(17), P1–Rh1–P2 177.11(4), P1–Rh1–C47 88.81(15), P2–Rh1–C47 88.43(15), Rh1–C47–O1 177.1(5). Cp denotes the center of the  $\eta^{5}$ -coordinated arene rings.

The rhodium(I) center in compound 4 is coordinated in a slightly distorted square-planar geometry with somewhat widened P–Rh1–Cl1 angles (91.53(4) and 91.28(4)°) due to the increased space requirement of the chloride ligand in comparison to the carbonyl ligand. The structural parameters overall resemble those measured for related complexes of the type  $CO(Cl)Rh(L)_2$  (L = phosphine ligand, *trans* orientation) in the past.<sup>18</sup>

The close structural relationship also allows a comparison of the energy of the CO stretching absorption in the infrared spectrum of **4** with data from the literature. This absorption is sensitive to the electronic situation at the rhodium(I) center, which is determined by two phosphine ligands. For compound 4 we measured a carbonyl band at 2002 cm<sup>-1</sup> (ATR). The conclusions that can be drawn from the position of this band on the electronic properties of ligand 1 are discussed in detail below.

In analogy to the reaction with  $[(\eta^6-p\text{-cymene})\text{MCl}_2]_2$  (M = Ru, Os), ligand 1 was treated with 1/2 equiv of the dimeric rhodium(III) and iridium(III) complexes  $[(\eta^5\text{-}C_5\text{Me}_5)\text{MCl}_2]_2$  (C<sub>5</sub>Me<sub>5</sub> = 1,2,3,4,5-pentamethylcyclopentadienyl, M = Rh, Ir).<sup>19</sup> Stirring these precursors with 1 in dichloromethane for 16 h led to the formation of **5** and **6** in 45% and 82% yields, respectively, after crystallization (Scheme 4).

Scheme 4. Synthesis of the Rhodium(III) and Iridium(III) Complexes 5 and  $6^a$ 



<sup>*a*</sup>Legend: (i)  $[(\eta^{5}-C_{5}Me_{5})MCl_{2}]_{2}$ , CH<sub>2</sub>Cl<sub>2</sub>, rt, 16 h.

The <sup>1</sup>H and <sup>13</sup>C NMR spectra show slightly broadened signals at room temperature, which may be the result of some hindered rotations due to the bulky Cp\* ring. The <sup>31</sup>P NMR supports the trend that was already observed for complexes **2** and **3**: whereas the phosphorus resonance of **5** is strongly shifted to lower field (33.7 ppm, <sup>1</sup> $J_{RhP}$  = 146.6 Hz) in comparison to that of **1** (-5.9 ppm), relativistic effects counteract that trend for **6** (3.2 ppm).

Recrystallization of the iridium(III) complex 6 by slow diffusion of diethyl ether into a saturated solution in dichloromethane gave single crystals suitable for a X-ray diffraction study. Figure 3 shows the molecular structure of 6 and summarizes typical bond parameters.

The solid-state structure of 6 generally resembles the structure of the ruthenium(II) complex 2. As a consequence of the higher oxidation state of the iridium center, the P1-Ir1



**Figure 3.** Molecular structure of compound **6** in the solid state. Characteristic bond lengths (Å) and angles (deg): Fe1–Cp 1.6700(12), Fe1–Ar 1.5298(12), Ir1–Cl1 2.4090(19), Ir1–Cl2 2.4065(19), Ir1–P1 2.3060(19), Ir1–Ar 1.8295(4), Cp–Fe1–Ar 177.76(9), Cl1–Ir1–Cl2 90.15(7), Cl1–Ir1–P1 89.92(7), Cl2–Ir1–P1 91.70(7), Cl1–Ir1–Ar 120.27(5), Cl2–Ir1–Ar 122.30(5), P1–Ir1–Cp 131.45(5). Cp denotes the center of the  $\eta^5$ -coordinated cyclopentadienyl ring. Ar denotes the centers of the  $\eta^6$ -coordinated arene rings.

bond length (2.3060(19) Å) is shorter in comparison to the P1–Ru1 bond (2.3590(9) Å), while the M–Cl bonds, which have more ionic character, are almost identical.

Analogous to the synthesis of the rhodium complex 4, treatment of 1 with 1 equiv of palladium(II) and platinum(II) chlorides resulted in the formation of the square-planar, dicationic complexes 7 and 8 (Scheme 5).

### Scheme 5. Synthesis of the Palladium(II) and Platinum(II) Complexes 7 and $8^a$



<sup>a</sup>Legend: (i) PdCl<sub>2</sub> or PtCl<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, rt, 16 h.

Both complexes were characterized by elemental analysis and ESI mass spectrometry. For the dication of complex 7 a peak at m/z 471.97 (calcd 471.99) and for the dication of complex 8 a peak at m/z 516.00 (calcd 516.01) were found. In addition, <sup>31</sup>P NMR spectroscopy proves the successful synthesis of compounds 7 and 8: aside from the typical heptet of the hexafluorophosphate anion (+144.6 ppm, <sup>1</sup> $J_{\rm PF}$  = 706 Hz), a singlet at +21.9 ppm is assigned to the palladium-bound phosphorus atom in complex 7. The resonance of the platinum-bound phosphorus site in complex 8 is observed at +17.6 ppm along with the expected <sup>195</sup>Pt satellites (<sup>1</sup> $J_{\rm PtP}$  = 2790 Hz).

While the *trans* orientation of the phosphine ligands in complex 7 was proved by X-ray structural analysis (Figure 4), the  $^{195}\text{Pt}-^{31}\text{P}$  coupling constant unambiguously assigns an identical geometry for complex 8. The literature reports e.g.  $^{195}\text{Pt}-^{31}\text{P}$  coupling constants of 3681 Hz for *cis*-(PPh<sub>3</sub>)<sub>2</sub>PtCl<sub>2</sub>



**Figure 4.** Molecular structure of compound 7 in the solid state. Characteristic bond lengths (Å) and angles (deg): Fe1–Cp 1.6744(5), Fe1–Ar 1.5447(5), Pd1–Cl1 2.2969(8), Pd1–P1 2.3270(7), Cp–Fe1–Ar 177.07(3), Cl1–Pd1–P1 92.51(3). Cp denotes the center of the  $\eta^{5}$ -coordinated cyclopentadienyl ring. Ar denotes the centers of the  $\eta^{6}$ -coordinated arene rings.

and of 2626 Hz for *trans*- $(PPh_3)_2PtCl_2$ .<sup>20</sup> A more detailed discussion of this coupling constant follows below. Single crystals of compound 7 that were suitable for an X-ray structure analysis were obtained by crystallization from nitromethane/diethyl ether at 5 °C. Figure 4 shows the molecular structure of 7 and summarizes typical bond parameters.

**Ligand Properties.** A first hint of the donor/acceptor properties of ligand 1 can be derived from the <sup>31</sup>P chemical shift and in particular from the <sup>195</sup>Pt-<sup>31</sup>P coupling constant measured for compound 8. Platinum(II) phosphine complexes of the type  $(PR_3)_2PtCl_2$  have been widely studied in the past. As has already been mentioned, the <sup>195</sup>Pt-<sup>31</sup>P coupling constant allows a determination of the coordination geometry of these compounds, since its value is much larger for the *cis* isomers in comparison to the *trans* isomers.<sup>20,21</sup>

Already in 1967, Grim, Keiter, and McFarlane published a NMR study on the influence of the phosphine substituents on the chemical shifts and <sup>195</sup>Pt-<sup>31</sup>P coupling constants of the *trans*-coordinated complexes  $(Ph_n(nBu)_{3-n}P)_2PtCl_2$  (n = 0, 1, 2).<sup>21b</sup> They found increasing values for the <sup>195</sup>Pt-<sup>31</sup>P coupling constant for increasing numbers of phenyl substituents (n = 0, n)2392 Hz; n = 1, 2462 Hz; n = 2, 2531 Hz). Their data fit well to the value for *trans*-(PPh<sub>3</sub>)<sub>2</sub>PtCl<sub>2</sub> (2626 Hz). Klein Gebbink and co-workers investigated the synthesis and spectroscopic data of *trans*-dichloridoplatinum complexes bearing the highly positively charged phosphine  $(P(C_6H_3(m-CH_2NMe_3)_2)_3)^{6+}$  in combination with different counteranions.<sup>20</sup> Depending on the solvent and the anions, coupling constants of 2627 Hz (Cl<sup>-</sup>/ DMSO- $d_6$ ), 2652 Hz (Cl<sup>-</sup>/D<sub>2</sub>O), and 2684 Hz (BF<sub>4</sub><sup>-</sup>/ DMSO) were found, indicating a minor influence of the positive charges on this value. In 1986 Brune and co-workers published a detailed study on the influence of ring-substituted triphenylphosphines  $(P(C_6H_{5-n}X_n)_3)$  (n = 1, 2) on the chemical shifts and the <sup>195</sup>Pt-<sup>31</sup>P coupling constants of platinum dichloride complexes.<sup>21a</sup> They found an excellent correlation of both the chemical shift and the coupling constant with the substituent constants  $\sigma$  of the Hammett equation.<sup>22</sup> The chemical shifts and the <sup>195</sup>Pt-<sup>31</sup>P coupling constants vary between +13.3 ppm/2534 Hz for the 4-NMe<sub>2</sub> substitution and +27.5 ppm/2787 Hz for the  $(3,5-CF_3)_2$ substitution.<sup>23</sup> Similar findings were later on reported by Pringle and co-workers.<sup>24</sup> For the *trans*-coordinated platinum dichloride complex bearing two perfluorinated triphenylphosphine ligands ( $P(C_6F_5)_3$ ) a chemical shift of -25.8 ppm and a <sup>195</sup>Pt $-^{31}$ P coupling constant of 3145 Hz were reported in the literature.<sup>23,25</sup> The substitution of one of the phenyl groups in PPh<sub>3</sub> by a bulky OAr unit raises the  ${}^{195}Pt - {}^{31}P$  coupling constant of the corresponding phosphinite complex trans-(Ph<sub>2</sub>POAr)<sub>2</sub>PtCl<sub>2</sub> up to 2887 Hz.<sup>26</sup> This value increases up to 4400 Hz for phosphite complexes of the type trans-((ArylO)<sub>3</sub>P)<sub>2</sub>PtCl<sub>2</sub>.<sup>26b,27</sup> The *trans*-configured platinum(II) phosphonite complex  $((RO)_2PR')_2PtCl_2$  has to the best of our knowledge not been reported in the literature. Thus, the value of 2790 Hz for the 195Pt-31P coupling constant of compound 8 is comparable to that of trans- $(P(C_6H_3(3,5 (CF_3)_2_3_2$ PtCl<sub>2</sub> but far away from the value of *trans*- $((P(C_6F_5)_3)_2PtCl_2$ . In contrast, the <sup>31</sup>P chemical shift (+17.6 ppm) is significantly lower than the value measured for trans- $(P(C_6H_3(3,5-CF_3)_2)_3)_2PtCl_2.$ 

Further details on the ligand properties of 1 can be obtained from the IR spectrum of the rhodium(I) complex 4. In the ATR-IR spectrum its carbonyl absorption is observed at 2002

cm<sup>-1</sup>, indicating a relatively large blue shift in comparison to the triphenylphosphine complex  $[RhCl(PPh_3)_2CO]$  (1978)  $cm^{-1}$ ),<sup>17</sup> which can be attributed to the influence of the cationic,  $\eta^6$ -coordinating cyclopentadienyl iron(II) arene site at the phosphine ligand. As already observed for the <sup>195</sup>Pt-<sup>31</sup>P coupling constant, the introduction of positively charged but not directly phenyl bound substituents in ligands such as  $(P(C_6H_3(m-CH_2NMe_3)_2)_3)^{6+}$  does not influence the CO absorption very much (1981 cm<sup>-1</sup>).<sup>28</sup> Compounds of the type  $[RhCl(PAr_3)_2CO]$  (Ar = para-substituted phenyl group) have been widely studied in the literature. The reported carbonyl absorptions range from approximately 1965  $cm^{-1}$  (p- $NMe_2$ ) to 1990 cm<sup>-1</sup> (p-CF<sub>3</sub>).<sup>29</sup> For the rhodium(I) complexes bearing two  $P(C_6F_5)_3$  or  $P(OMe)_3$  ligands values of 2005 and 2005 cm<sup>-1</sup>, respectively, were found. In 2011 Sakai and co-workers reported the synthesis of the extremely electron poor 2,6-bis(trifluoromethyl)-4-pyridyl group into phosphines.<sup>30</sup> For the carbonylchloridorhodium(I) complex bearing two (2,6-bis(trifluoromethyl)-4-pyridyl)diphenylphosphine ligands they measured 2017 cm<sup>-1</sup> for the CO stretching vibration.

To get further insights into the steric and electronic properties of the cationic phosphine ligand 1, we investigated its Tolman steric parameter (TSP) and the Tolman electronic parameter (TEP)<sup>2</sup> by density functional theory (DFT) at the B3LYP level using the Def2-TZVP basis set (see the Supporting Information for details). Subsequent to the determination of the calculated electronic parameter (CEP) for the hypothetical cationic complex  $[(1)Ni(CO)_3]^+$ , the TEP was estimated by the utilization of the scaling factor (0.968) reported by Duncan et al. for transition-metal carbonyl complexes.<sup>31</sup> The same was done for the previously reported, related phosphines **A**, **B** and **Ca–Cc** and the corresponding, spectroscopically characterized tricarbonylnickel(0) complexes (Scheme 6 and Table 1, entries 1–5)), to evaluate the method.<sup>7a,32</sup>

Scheme 6. Phosphine Ligands Used for the Comparison of TSP, CEP, and TEP Data with Ligand 1



Table 1. TSP, CEP, and TEP data Calculated for the Ni(CO)<sub>3</sub> Complexes of Ligands A, B, Ca-Cc, and 1

entry	ligand	exptl TSP (deg)	CEP $(cm^{-1})$	exptl TEP (cm <sup>-1</sup> )
1	Α	135 (133) <sup>a</sup>	2129	2061 (2066) <sup>a</sup>
2	В	172	2140	$2071 (2074)^{b}$
3	Ca	129	2158	$2089 (2082)^c$
4	Cb	140	2154	$2085 (2078)^c$
5	Cc	121	2152	$2083 (2075)^c$
6	1	132	2150	2081
7	$PPh_3$	$124 (145)^d$	2132	$2064 \ (2069)^d$
<sup>a</sup> See ref 32a. <sup>b</sup> See ref 32b. <sup>c</sup> See ref 7a. <sup>d</sup> See ref 2.				

Calculated values of the TEPs are within the expected error  $(RMS = 7.5 \text{ cm}^{-1})^{30}$  of the calculation. Only the TEP of Cc is

slightly out of this range (Table 1, entry 5). Nevertheless, our calculations correctly reflect the experimentally observed trend within the series of A, B, and Ca-Cc. The applied computational method should therefore provide reliable results for a differentiation among the different types of phosphines analyzed. In addition, the calculations show a satisfying accuracy, independently of the charge of the complex.

Ligand 1 is therefore characterized by a TSP similar to that of ferrocenyldiphenylphosphine (A) but significantly smaller than that of **B**. In contrast, the predicted TEP value of 1 is substantially higher in comparison to those of **A** and **B** and comes close to the data of Ca–Cc. These results underline its acceptor properties. With its calculated TSP (132°) and TEP (2081 cm<sup>-1</sup>) values, ligand 1 is within an area of the Tolman stereoelectronic map that is traditionally covered by phosphites,<sup>2</sup> which is in complete agreement with the spectroscopic data (<sup>195</sup>Pt–<sup>31</sup>P coupling constant, carbonyl absorption) measured for complexes 8 and 4. This might open up opportunities for applications in catalytic transformations that are performed with phosphites by avoiding e.g. the moisture sensitivity of these compounds.

**Catalysis.** To prove the applicability of ligand 1 in catalytic reactions, we have investigated compound 2 for the transfer hydrogenation of acetophenone with isopropyl alcohol as the hydrogen source as well as for the isomerization of estragole leading to anethole.

The complex  $[(\eta^6\text{-}p\text{-}cymene)\operatorname{Ru}(\operatorname{Cl})_2(\operatorname{PPh}_3)]$  has been described to catalyze the transfer hydrogenation of acetophenone with medium activity.<sup>33</sup> We have carried out the reaction under the conditions reported in the Experimental Section. While  $[(\eta^6\text{-}p\text{-}cymene)\operatorname{Ru}(\operatorname{Cl})_2(\operatorname{PPh}_3)]$  gave 81% conversion of the substrate after 3 h, complex 2 led to only 2% conversion. Prolonging the reaction time to 20 h resulted in 7% conversion. These results can be explained by the mechanism of the transfer hydrogenation process, which includes the transfer of a hydrido ligand to the substrate, which will be more difficult due to the positive charge of complex 2.

In the second reaction we investigated the isomerization of the allylic substrate estragole to the styrene derivative anethole. Here we compared compound **2** with both  $[(\eta^6-p\text{-}cymene)\text{-}Ru(Cl)_2(PPh_3)]$  and  $[(\eta^6-p\text{-}cymene)\text{-}Ru(Cl)_2(P(OMe)_3)]$ . Both complexes were reported to be highly active in this reaction.<sup>34</sup> Here complex **2** performs better than in the transfer hydrogenation, giving 71% conversion under the conditions described in the Experimental Section. However, the other two complexes provided the product in yields >99%. Here, the electron deficiency of the ligand seems not to decrease the activity of the ruthenium complex as dramatically as in the transfer hydrogenation. The poorer activity in comparison to the trimethyl phosphite complex could be a result of steric factors.

#### CONCLUSION

Novel cationic multimetallic complexes bearing the ligand ( $\eta^6$ diphenylphosphinobenzene)( $\eta^5$ -cyclopentadienyl)iron(II) hexafluorophosphate (1) were obtained with transition metals of groups XIII–X and completely characterized. The donor/ acceptor properties of the cationic phosphine were determined on the basis of spectroscopic data ( $^{195}$ Pt– $^{31}$ P coupling constant, carbonyl IR absorption) as well as of theoretical calculations. The data point out that compound 1 behaves electronically more or less like a phosphite, meaning that it is a weaker  $\sigma$  donor and a stronger  $\pi$  acceptor in comparison to common triarylphosphines. We are currently investigating some catalytic reactions, for which phosphites are typically used, to further substantiate our results in terms of reactivity.

#### EXPERIMENTAL SECTION

Ligand 1 was synthesized according to a procedure reported in the literature.<sup>11</sup> All reactions were carried out under an argon atmosphere using standard Schlenk techniques. The solvents were either freshly distilled or dried and degassed before use according to standard techniques. Commercially available chemicals were purchased from ABCR, Alfa Aesar, Sigma-Aldrich, Strem, or TCI. <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra were recorded on Bruker Spectrospin Avance 400 and 600 spectrometers. The chemical shifts are referenced to internal solvent resonances. The multiplicities are reported as s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, and m = multiplet. The NMR spectra of the iron complexes generally show slightly broadened resonances. This might be due to some paramagnetic impurities and hinders the assignment of P,C-coupling constants in some cases. Infrared spectra were recorded on a JASCO FT/IK-6100 spectrometer using attenuated total reflection. ESI-mass spectrometric measurements were performed on an AmaZon ETD instrument by introducing solutions of the compound in acetonitrile. Elemental analyses were carried out with a Vario MICRO Cube elemental analyzer at the Analytical Laboratory of the Technische Universität Kaiserslautern. For the X-ray structural analyses and for computational details please refer to the Supporting Information.

Dichlorido ( $(\eta^5 - cyclopentadienyl)$ ) ( $\eta^6$ diphenylphosphinobenzene)iron(II)) $(\eta^6$ -p-cymene)ruthenium-(II) Hexafluorophosphate (2). A 200 mg portion (0.33 mmol) of bis(dichlorido( $\eta^6$ -*p*-cymene)ruthenium(II))<sup>12a</sup> and 345 mg (0.66 mmol) of 1 were dissolved in 10 mL of CH<sub>2</sub>Cl<sub>2</sub>, and the mixture was stirred for 16 h at room temperature. The solvent was removed under vacuum, and the crude product was washed with 10 mL of Et<sub>2</sub>O, yielding 492 mg (90%) of 2 as an orange powder. Crystallization from CH2Cl2/Et2O gave orange crystals. Anal. Calcd for C<sub>33</sub>H<sub>34</sub>Cl<sub>2</sub>F<sub>6</sub>FeP<sub>2</sub>Ru: C, 47.50; H, 4.11. Found: C, 47.07; H, 4.18. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): δ 7.99–7.84 (m, 4H), 7.62 (m, 6H), 6.90 (s, 2H), 6.22 (m, 3H), 5.46 (d, J = 5.7 Hz, 1H), 5.25 (d, J = 6.1 Hz, 2H), 4.35 (s, 5H), 2.34 (sept, 1H), 1.88 (s, 3H), 0.79 (d, J = 6.9 Hz, 6H) ppm. <sup>13</sup>C NMR (151 MHz, CD<sub>3</sub>CN): δ 135.6, 135.0, 132.8, 129.7, 110.3, 98.9, 97.4, 95.6, 92.54, 88.7, 87.7, 87.3, 78.7, 30.8, 21.4, 17.4 ppm. <sup>31</sup>P NMR (162 MHz, CD<sub>3</sub>CN): δ 27.5 (s), -144.6 (sept, J = 706.5 Hz) ppm. ESI-MS ( $CD_3CN$ ): m/z 688.94 [ $C_{33}H_{34}Cl_2FePRu$ ]<sup>+</sup>.

D i c h l o r i d o ( ( $\eta^{5}$  - c y c l o p e n t a d i e n y l ) ( $\eta^{6}$  - diphenylphosphinobenzene)iron(II))( $\eta^{6}$ -p-cymene)osmium(II) Hexafluorophosphate (3). This complex was synthesized as for compound 2 with 47.4 mg (0.06 mmol) of bis(dichlorido( $\eta^{6}$ -p-cymene)osmium(II))<sup>12b</sup> and 63.4 mg (0.12 mmol) of 1. Yield: 77.0 mg (70%) of an orange microcrystalline solid. Anal. Calcd for C<sub>33</sub>H<sub>34</sub>Cl<sub>2</sub>F<sub>6</sub>FeP<sub>2</sub>Os: C, 42.92; H, 3.71. Found: C, 42.48; H, 3.67. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):  $\delta$  7.90–7.76 (m, 4H), 7.65–7.53 (m, 6H), 7.03 (m, 2H), 6.25 (m, 3H), 5.60 (d, J = 5.5 Hz, 2H), 5.46 (d, J = 6.0 Hz, 1H), 4.37 (s, 5H), 1.97 (s, 3H), 0.83 (d, J = 6.9 Hz, 6H) ppm. <sup>13</sup>C NMR (151 MHz, CD<sub>3</sub>CN):  $\delta$  135.3, 135.0, 132.8, 129.6, 101.6, 99.3, 95.5, 90.3, 88.8, 87.4, 84.6, 80.8, 78.7, 30.4, 21.8, 17.1 ppm. <sup>31</sup>P NMR (162 MHz, CD<sub>3</sub>CN):  $\delta$  –15.6 (s), –144.6 (sept, J = 706.5 Hz) ppm. ESI-MS (CD<sub>3</sub>CN): m/z = 779.06 [C<sub>33</sub>H<sub>34</sub>cl<sub>2</sub>FePOs]<sup>+</sup>.

**Carbonylchlorido(bis(**( $\eta^{5}$ -cyclopentadienyl)( $\eta^{6}$ diphenylphosphinobenzene)iron(II)))rhodium(I) Bis-(hexafluorophosphate) (4). Stirring a solution of 50.0 mg (0.13 mmol) of bis(dicarbonyl( $\mu_{2}$ -chlorido)rhodium(I)),<sup>16</sup> 100 mg (0.54 mmol) of KPF<sub>6</sub>, and 273 mg (0.52 mmol) of 1 in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> for 16 h at room temperature resulted in a yellow suspension. After decanting of the solvent, the crude product was dissolved in 10 mL of CH<sub>3</sub>CN and the insoluble components were filtered off. The solvent was removed under vacuum to give 312 mg (99%) of a yellow microcrystalline solid, which was recrystallized from CH<sub>3</sub>CN/Et<sub>2</sub>O. Anal. Calcd for C<sub>47</sub>H<sub>40</sub>ClF<sub>12</sub>Fe<sub>2</sub>OP<sub>4</sub>Rh: C, 46.17; H, 3.30. Found: C, 45.93; H, 3.22. <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>CN): δ 7.77 (s, 8H), 7.64 (t, J = 7.4 Hz, 4H), 7.58 (t, J = 7.6 Hz, 8H), 6.68 (s, 4H), 6.47 (t, J = 6.2 Hz, 2H), 6.39 (t, J = 6.4 Hz, 4H), 5.03 (s, 10H) ppm. <sup>13</sup>C NMR (151 MHz, CD<sub>3</sub>CN): δ 135.5, 133.1, 131.5, 130.2, 98.2, 93.2, 89.9, 89.2, 79.3 ppm. <sup>31</sup>P NMR (162 MHz, CD<sub>3</sub>CN): δ 26.9 (d, J = 131.0 Hz), -144.6 (sept, J = 706.6 Hz) ppm. IR (ATR): ν 3117 (w), 3069 (w), 2002 (s), 1483 (w), 1437 (w), 1420 (w), 1312 (w), 1285 (w), 1093 (w), 823 (s), 749 (w), 693 (m), 555 (s), 517 (w) cm<sup>-1</sup>. **Dichlorido((** $\eta$ <sup>5</sup>-cyclopentadienyl)( $\eta$ <sup>6</sup>-

Dichlorid o (( $\eta^{5}$ -cyclopentadienyl)( $\eta^{6}$ -diphenylphosphinobenzene)iron(II))( $\eta^{5}$ -1,2,3,4,5pentamethylcyclopentadienyl)rhodium(III) Hexafluorophosphate (5). A 62.4 mg portion (0.10 mmol) of bis(dichlorido( $\eta^{5}$ -1,2,3,4,5-pentamethylcyclopentadienyl)rhodium(III))<sup>19</sup> and 106 mg (0.20 mmol) of 1 were stirred for 16 h in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> at room temperature. The solvent was removed under vacuum, and the crude product was washed with 10 mL of Et<sub>2</sub>O. Slow diffusion of Et<sub>2</sub>O into a saturated solution of 5 in CH<sub>2</sub>Cl<sub>2</sub> gave 75 mg (45%) of an orange microcrystalline solid. Anal. Calcd for C<sub>33</sub>H<sub>35</sub>Cl<sub>2</sub>F<sub>6</sub>FeP<sub>2</sub>Rh: C, 47.34; H, 4.21. Found: C, 47.19; H, 4.06. <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>CN):  $\delta$ 8.02 (s, 4H), 7.73–7.56 (m, 6H), 7.00 (s, 2H), 6.24 (s, 3H), 4.39 (s, 5H), 1.28 (d, *J* = 3.9 Hz, 15H) ppm. <sup>13</sup>C NMR (151 MHz, CD<sub>3</sub>CN):  $\delta$  135.3, 133.2, 131.7, 129.8, 101.4, 96.1, 88.7, 87.2, 78.7, 88 ppm. <sup>31</sup>P NMR (243 MHz, CD<sub>3</sub>CN):  $\delta$  33.7 (d, *J* = 146.6 Hz), -144.6 (sept, *J* = 706.5 Hz) ppm.

Dichlorido ( $(\eta^{5} - cyclopentadienyl)(\eta^{6} - diphenylphosphinobenzene)iron(II))(\eta^{5} - 1,2,3,4,5-pentamethylcyclopentadienyl)iridium(III) Hexafluorophosphate (6). This complex was synthesized as for compound 5 with 200 mg (0.25 mmol) of bis(dichlorido(<math>\eta^{5} - 1,2,3,4,5$ -pentamethylcyclopentadienyl)iridium(III))<sup>19</sup> and 265 mg (0.50 mmol) of 1. Yield: 390 mg (82%), orange microcrystalline solid. Recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O. Anal. Calcd for C<sub>33</sub>H<sub>35</sub>Cl<sub>2</sub>F<sub>6</sub>FeP<sub>2</sub>Ir: C, 42.78; H, 3.81. Found: C, 42.51; H, 3.52. <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>CN):  $\delta$  7.96 (s, 4H), 7.61 (s, 6H), 7.03 (s, 2H), 6.28 (s, 3H), 4.41 (s, 5H), 1.26 (s, 15H) ppm. <sup>13</sup>C NMR (151 MHz, CD<sub>3</sub>CN):  $\delta$  135.2, 133.1, 132.1, 129.6, 95.4, 95.1, 88.9, 87.4, 78.7, 8.3 ppm. <sup>31</sup>P NMR (243 MHz, CD<sub>3</sub>CN):  $\delta$  3.2 (s), -144.6 (sept, J = 706.6 Hz) ppm. ESI-MS (CD<sub>3</sub>CN): m/z 780.98 [C<sub>33</sub>H<sub>35</sub>Cl<sub>2</sub>FePIr]<sup>+</sup>.

Dichlorido (bis ( $\eta^5$ -cyclopentadienyl) ( $\eta^6$ diphenylphosphinobenzene)iron(II))palladium(II) Bis-(hexafluorophosphate) (7). A 44.3 mg portion (0.25 mmol) of palladium dichloride and 264 mg (0.50 mmol) of 1 were dissolved in 10 mL of CH<sub>2</sub>Cl<sub>2</sub>, and this mixture was stirred for 16 h at room temperature to give a beige suspension. After removal of the solvent under vacuum, the crude product was crystallized from CH<sub>3</sub>NO<sub>2</sub>/ Et<sub>2</sub>O at 5 °C. Yield: 242 mg (79%) of beige crystals. Anal. Calcd for C<sub>46</sub>H<sub>40</sub>Cl<sub>2</sub>F<sub>12</sub>Fe<sub>2</sub>P<sub>4</sub>Pd: C, 44.78; H, 3.27. Found: C, 44.93; H, 3.25. <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>NO<sub>2</sub>):  $\delta$  7.98–7.88 (m, 8H), 7.69 (m, 12H), 6.76 (s, 4H), 6.60 (s, 2H), 6.51 (t, *J* = 5.8 Hz, 4H), 5.06 (s, 10H) ppm. <sup>13</sup>C NMR (151 MHz, CD<sub>3</sub>NO<sub>2</sub>):  $\delta$  135.0, 132.5, 129.0, 126.8, 95.4, 92.2, 88.9, 87.9, 78.4 ppm. <sup>31</sup>P NMR (162 MHz, CD<sub>3</sub>NO<sub>2</sub>):  $\delta$  21.9 (s), -144.6 (sept, *J* = 706.5 Hz) ppm. ESI-MS (DMSO): m/z 471.96 [C<sub>46</sub>H<sub>40</sub>Cl<sub>2</sub>Fe<sub>2</sub>P<sub>2</sub>Pd]<sup>2+</sup>.

(DMSO): m/z 471.96 [C<sub>46</sub>H<sub>40</sub>Cl<sub>2</sub>Fe<sub>2</sub>P<sub>2</sub>Pd]<sup>2+</sup>. **Dichlorido** (**bis** ( $\eta^{5}$  - **cyclopentadien**) (1) ( $\eta^{6}$  - **diphenylphosphinobenzene**)iron(II))platinum(II) **Bis-(hexafluorophosphate)** (8). This complex was synthesized as for compound 7 with 40.0 mg (0.15 mmol) of platinum dichloride and 158 mg (0.30 mmol) of 1. Recrystallization from CH<sub>3</sub>CN/Et<sub>2</sub>O. Yield: 147 mg (74%) of a beige microcrystalline solid. Anal. Calcd for C<sub>46</sub>H<sub>40</sub>Cl<sub>2</sub>F<sub>12</sub>Fe<sub>2</sub>P<sub>4</sub>Pt: C, 41.78; H, 3.05. Found: C, 41.93; H, 3.03. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>NO<sub>2</sub>):  $\delta$  7.93 (dd, J = 12.7, 6.2 Hz, 8H), 7.69 (dt, J = 24.9, 7.2 Hz, 12H), 6.79 (dt, J = 6.5, 3.3 Hz, 4H), 6.61 (t, J = 6.1 Hz, 2H), 6.53 (t, J = 6.3 Hz, 4H), 5.10 (s, 10H) ppm. <sup>13</sup>C NMR (151 MHz, CD<sub>3</sub>NO<sub>2</sub>):  $\delta$  135.5, 133.0, 129.4, 126.3, 95.0, 92.5, 89.5, 88.5, 78.9 ppm. <sup>31</sup>P NMR (162 MHz, CD<sub>3</sub>NO<sub>2</sub>):  $\delta$  17.6 (s), -144.6 (sept, J = 706.5 Hz) ppm. ESI-MS (CD<sub>3</sub>CN): m/z 516.00 [C<sub>46</sub>H<sub>40</sub>-Cl<sub>2</sub>Fe<sub>2</sub>P<sub>2</sub>Pt]<sup>2+</sup>.

General Procedure for the Catalytic Transfer Hydrogenation. The ruthenium catalyst (0.01 mmol) and KOH (4.95 mg, 0.075 mmol) were dissolved in isopropyl alcohol (5 mL) in a crimp-cap vial. Then acetophenone (120 mg, 1.00 mmol, 117  $\mu$ L) was added at a temperature of 80 °C. Samples were taken after 3 and 20 h with single-use syringes, filtered through a short column filled with a small amount of neutral aluminum oxide and MgSO<sub>4</sub>, eluted with ethyl acetate, and analyzed by gas chromatography.

General Procedure for the Isomerization of Estragole. Either 2 (16.7 mg, 0.02 mmol) or bis(dichlorido( $\eta^6$ -*p*-cymene)ruthenium-(II)) (6.12 mg, 0.01 mmol) and the corresponding phosphine or phosphite (0.02 mmol) were dissolved in methanol (0.5 mL) in a crimp-cap vial. Then estragole (302 mg, 2.00 mmol, 315  $\mu$ L) was added at a temperature of 80 °C. Samples were taken after 24 h with single-use syringes, filtered through a short column filled with a small amount of neutral aluminum oxide and MgSO<sub>4</sub>, eluted with deuterated chloroform, and analyzed by NMR spectroscopy.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00414.

NMR, IR, and ESI-MS spectra, crystallographic data, and computational details (PDF)

Cartesian coordinates of the calculated structures (XYZ)

#### Accession Codes

CCDC 2006876–2006879 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

#### AUTHOR INFORMATION

#### **Corresponding Author**

Werner R. Thiel – Fachbereich Chemie, Technische Universität Kaiserslautern, 67663 Kaiserslautern, Germany; orcid.org/ 0000-0001-5283-2368; Email: thiel@chemie.uni-kl.de

#### Authors

- Christian Malchau Fachbereich Chemie, Technische Universität Kaiserslautern, 67663 Kaiserslautern, Germany Florian Loose – Fachbereich Chemie, Technische Universität
- Kaiserslautern, 67663 Kaiserslautern, Germany
- Yannick Mees Fachbereich Chemie, Technische Universität Kaiserslautern, 67663 Kaiserslautern, Germany; Research Center OPTIMAS, D-67663 Kaiserslautern, Germany
- Jens Duppe Fachbereich Chemie, Technische Universität Kaiserslautern, 67663 Kaiserslautern, Germany
- Yu Sun Fachbereich Chemie, Technische Universität Kaiserslautern, 67663 Kaiserslautern, Germany
- Gereon Niedner-Schatteburg Fachbereich Chemie, Technische Universität Kaiserslautern, 67663 Kaiserslautern, Germany; Research Center OPTIMAS, D-67663 Kaiserslautern, Germany; © orcid.org/0000-0001-7240-6673

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.organomet.0c00414

#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

The authors wish to thank the DFG-funded transregional collaborative research center SFB/TRR 88 "Cooperative effects in homo- and heterometallic complexes (3MET" for financial support.

#### REFERENCES

(1) (a) Homogeneous Catalysis with Metal Phosphine Complexes; Pignolet, L. M., Ed.; Springer: Berlin, 1983. (b) Catalytic Aspects of Metal Phosphine Complexes; Alyea, E. C., Meek, D. W., Eds.; American Chemical Society: Washington, DC, 1982. (c) Phosphorus(III) Ligands in Homogeneous Catalysis: Design and Synthesis; Kamer, P. C. J., van Leeuwen, P. W. N. M., Eds.; Wiley: Hoboken, NJ, 2012.

(2) (a) Tolman, C. A. Electron donor-acceptor properties of phosphorus ligands. Substituent additivity. J. Am. Chem. Soc. 1970, 92, 2953–2956. (b) Tolman, C. A. Steric effects of phosphorus ligands in organometallic chemistry and homogeneous catalysis. Chem. Rev. 1977, 77, 313–348.

(3) (a) Nicholls, L. D. M.; Alcarazo, M. Applications of  $\alpha$ -Cationic Phosphines as Ancillary Ligands in Homogeneous Catalysis. *Chem. Lett.* **2019**, 48, 1–13. (b) Korenaga, T.; Sasaki, R.; Shimada, K. Highly electron-poor Buchwald-type ligand: application for Pd-catalysed direct arylation of thiophene derivatives and theoretical consideration of the secondary Pd(0)-arene interaction. *Dalton Trans.* **2015**, 44, 19642–19650. (c) Pollock, C. L.; Saunders, G. C.; Smyth, E.C.M. S.; Sorokin, V. I. Fluoroarylphosphines as ligands. *J. Fluorine Chem.* **2008**, 129, 142–166. (d) Alcarazo, M.  $\alpha$ -Cationic phosphines: synthesis and applications. *Chem. - Eur. J.* **2014**, 20, 7868–7877. (e) Alcarazo, M. Synthesis, Structure, and Applications of  $\alpha$ -Cationic Phosphines. *Acc. Chem. Res.* **2016**, 49, 1797–1805. (f) Abe, K.; Kitamura, M.; Fujita, H.; Kunishima, M. Development of highly electron-deficient and less sterically-hindered phosphine ligands possessing 1,3,5-triazinyl groups. *Mol. Catal.* **2018**, 445, 87–93.

(4) (a) Gual, A.; Godard, C.; de la Fuente, V.; Castillón, S. Design and Synthesis of Phosphite Ligands for Homogeneous Catalysis. In ref 1c. (b) Fernández-Pérez, H.; Etayo, P.; Panossian, A.; Vidal-Ferran, A. *Chem. Rev.* **2011**, *111*, 2119–2176.

(5) (a) Drews, T.; Rusch, D.; Seidel, S.; Willemsen, S.; Seppelt, K. Systematic reactions of Pt(PF<sub>3</sub>)<sub>4</sub>. Chem. - Eur. J. 2008, 14, 4280-4286. (b) Kruck, T. Trifluorophosphine complexes of transition metals. Angew. Chem., Int. Ed. Engl. 1967, 6, 53-67. (c) Nixon, J. F. Trifluorophosphine complexes of transition metals. Adv. Inorg. Chem. 1985, 29, 41-141. (d) Mathieu, R.; Lenzi, M.; Poilblanc, R. Phosphorus-31 nuclear magnetic resonance study of trivalent phosphorus derivatives of metal carbonyls. Inorg. Chem. 1970, 9, 2030–2034. (e) Rycroft, D. S.; Sharp, D. W. A.; Wright, J. G. Mixed trihalophosphine complexes of nickel(0) and platinum(II). Inorg. Nucl. Chem. Lett. 1978, 14, 451-455. (f) Davies, M. S.; Pierens, R. K.; Aroney, M. J. Metal-ligand bonding in LM(CO)<sub>5</sub> complexes (L =  $NMe_{3}$ ,  $PMe_{3}$ ,  $PCl_{3}$ ,  $PBr_{3}$  or  $AsMe_{3}$ ; M = Cr, Mo or W) from dielectric, electro-optic and spectroscopic evidence. J. Organomet. Chem. 1993, 458, 141-146. (g) Frenking, G.; Wichmann, K.; Fröhlich, N.; Grobe, J.; Golla, W.; Van, D. L.; Krebs, B.; Läge, M. Nature of the Metal-Ligand Bond in  $M(CO)_5PX_3$  Complexes (M = Cr, Mo, W; X = H, Me, F, Cl): Synthesis, Molecular Structure, and Quantum-Chemical Calculations. Organometallics 2002, 21, 2921-2930.

(6) Bennett, F. W.; Brandt, G. R. A.; Emeleus, H. J.; Haszeldine, R. N. Trifluoromethyl derivatives of phosphorus, arsenic and sulphur. *Nature* **1950**, *166*, 225.

(7) (a) Azouri, M.; Andrieu, J.; Picquet, M.; Richard, P.; Hanquet, B.; Tkatchenko, I. Straightforward Synthesis of Donor-Stabilised Phosphenium Adducts from Imidazolium-2-carboxylate and Their Electronic Properties. *Eur. J. Inorg. Chem.* 2007, 2007, 4877–4883.
(b) Burford, N.; Losier, P.; Phillips, A. D.; Ragogna, P. J.; Cameron, T. S. Nitrogen ligands on phosphorus(III) Lewis acceptors: A versatile new synthetic approach to unusual N-P structural arrangements. *Inorg. Chem.* 2003, 42, 1087–1091. (c) Burford, N.; Ragogna, P. J.; McDonald, R.; Ferguson, M. J. Phosphine coordination complexes of the diphenylphosphenium cation: a versatile synthetic methodology for P-P bond formation. *J. Am. Chem. Soc.* 2003, 125, 14404–14410. (d) Kuhn, N.; Fahl, J.; Bläser, D.; Boese, R. Synthese und Eigenschaften von [Ph<sub>2</sub>(Carb)P]AlCl<sub>4</sub> (Carb = 2,3-Dihydro-1,3-diisopropyl-4,5-dimethylimidazol-2-yliden) - ein stabiler Carben-Komplex des dreiwertigen Phosphors [1]. *Z. Anorg. Allg. Chem.*

**1999**, 625, 729–734. (e) Kuhn, N.; Henkel, G.; Göhner, M.  $\{Ph_2(Carb)P\}MCl_3$  (M = Pd, Pt; Carb = 2,3-dihydro-1,3-diisopropyl-4,5dimethylimidazol-2-ylidene) - a Novel Cationic Phosphane Ligand [1]. *Z. Anorg. Allg. Chem.* **1999**, 625, 1415–1416.

(8) (a) Petuškova, J.; Bruns, H.; Alcarazo, M. Cyclopropenylylidenestabilized diaryl and dialkyl phosphenium cations: applications in homogeneous gold catalysis. *Angew. Chem., Int. Ed.* **2011**, *50*, 3799– 3802. (b) Petuškova, J.; Patil, M.; Holle, S.; Lehmann, C. W.; Thiel, W.; Alcarazo, M. Synthesis, structure, and reactivity of carbenestabilized phosphorus(III)-centered trications  $[L_3P]^{3+}$ . *J. Am. Chem. Soc.* **2011**, *133*, 20758–20760.

(9) (a) Sirieix, J.; Oßberger, M.; Betzemeier, B.; Knochel, P. Palladium Catalyzed Cross-Couplings of Organozincs in Ionic Liquids. Synlett 2000, 1613-1615. (b) Wan, Q.-X.; Liu, Y.; Lu, Y.; Li, M.; Wu, H.-H. Palladium-Catalyzed Heck Reaction in the Multi-Functionalized Ionic Liquid Compositions. Catal. Lett. 2008, 121, 331-336. (c) Brasse, C. C.; Englert, U.; Salzer, A.; Waffenschmidt, H.; Wasserscheid, P. Ionic Phosphine Ligands with Cobaltocenium Backbone: Novel Ligands for the Highly Selective, Biphasic, Rhodium-Catalyzed Hydroformylation of 1-Octene in Ionic Liquids. Organometallics 2000, 19, 3818-3823. (d) Brauer, D. J.; Kottsieper, K. W.; Liek, C.; Stelzer, O.; Waffenschmidt, H.; Wasserscheid, P. Phosphines with 2-imidazolium and para-phenyl-2-imidazolium moieties-synthesis and application in two-phase catalysis. J. Organomet. Chem. 2001, 630, 177-184. (e) Li, J.; Peng, J.; Bai, Y.; Zhang, G.; Lai, G.; Li, X. Phosphines with 2-imidazolium ligands enhance the catalytic activity and selectivity of rhodium complexes for hydrosilylation reactions. J. Organomet. Chem. 2010, 695, 431-436. (f) Chen, S.-J.; Li, Y.-Q.; Wang, P.; Lu, Y.; Zhao, X.-L.; Liu, Y. Promotion effect of water on hydroformylation of styrene and its derivatives with presence of amphiphilic zwitterionic phosphines. J. Mol. Catal. A: Chem. 2015, 407, 212-220. (g) Chen, S.-J.; Li, Y.-Q.; Wang, Y.-Y.; Zhao, X.-L.; Liu, Y. Ionic Rh(I)-complexes containing  $\pi$ accepting and hemilabile P,N-ligands as efficient catalysts for hydroformylation of 1-octene. J. Mol. Catal. A: Chem. 2015, 396, 68-76. (h) Chen, S.-J.; Wang, Y.-Y.; Yao, W.-M.; Zhao, X.-L.; VO-Thanh, G.; Liu, Y. An ionic phosphine-ligated rhodium(III) complex as the efficient and recyclable catalyst for biphasic hydroformylation of 1-octene. J. Mol. Catal. A: Chem. 2013, 378, 293-298. (i) Li, Y.-Q.; Liu, H.; Wang, P.; Yang, D.; Zhao, X.-L.; Liu, Y. Immobilization of a rhodium catalyst using a diphosphine-functionalized ionic liquid in RTIL for the efficient and recyclable biphasic hydroformylation of 1octene. Faraday Discuss. 2016, 190, 219-230. (j) You, H.; Wang, Y.; Zhao, X.; Chen, S.; Liu, Y. Stable Ionic Rh(I,II,III) Complexes Ligated by an Imidazolium-Substituted Phosphine with  $\pi$ -Acceptor Character: Synthesis, Characterization, and Application to Hydroformylation. Organometallics 2013, 32, 2698-2704. (k) Zhang, H.; Li, Y.-Q.; Wang, P.; Lu, Y.; Zhao, X.-L.; Liu, Y. Effect of positive-charges in diphosphino-imidazolium salts on the structures of Ir-complexes and catalysis for hydroformylation. J. Mol. Catal. A: Chem. 2016, 411, 337-343. (1) Gu, L.; Wolf, L. M.; Zieliński, A.; Thiel, W.; Alcarazo, M.  $\alpha$ -Dicationic Chelating Phosphines: Synthesis and Application to the Hydroarylation of Dienes. J. Am. Chem. Soc. 2017, 139, 4948-4953.

(10) Dabirmanesh, Q.; Fernando, S. I. S.; Roberts, R. M. G. Synthesis and decomplexation of  $(\eta$ -arene) $(\eta$ -cyclopentadienyl)-iron(II) hexafluorophosphates using microwave dielectric heating. *J. Chem. Soc., Perkin Trans.* 1 **1995**, *46*, 743–749.

(11) Eger, T. R.; Munstein, I.; Steiner, A.; Sun, Y.; Niedner-Schatteburg, G.; Thiel, W. R. New cationic organometallic phosphane ligands and their coordination to gold(I). *J. Organomet. Chem.* **2016**, *810*, 51–56.

(12) (a) Bennett, M. A.; Smith, A. K. Arene Ruthenium(II) Complexes formed by Dehydrogenation of Cyclohexadienes with Ruthenium(III) Trichloride. *J. Chem. Soc., Dalton Trans.* **1974**, 233– 241. (b) Werner, H.; Zenkert, K. Aromaten(Phosphan)metall-Komplexe XIII \*. Osmium(2)- und Osmium(O)-Komplexe mit p-Cymen als aromatischem Liganden. *J. Organomet. Chem.* **1988**, 345, 151–166. (13) (a) Serron, S. A.; Nolan, S. P. Enthalpies of Reaction of ((pcymene)RuCl<sub>2</sub>)<sub>2</sub> with Monodentate Tertiary Phosphine Ligands. Importance of both Steric and Electronic Ligand Factors in a Ruthenium(II) System. Organometallics **1995**, 14, 4611–4616. (b) Huang, J.; Serron, S.; Nolan, S. P. Enthalpies of Reaction of [(p-cymene)OsCl<sub>2</sub>]<sub>2</sub> with Monodentate Tertiary Phosphine Ligands. Importance of Steric and Electronic Ligand Factors in an Osmium(II) System. Organometallics **1998**, 17, 4004–4008.

(14) Grim, S. O.; Yankowsky, A. W. Phosphorus-31 Nuclear Magnetic Resonance Studies on Hydrobromides of Substituted Triarylphosphines and Other Derivatives. *J. Org. Chem.* **1977**, *42*, 1236–1239.

(15) Elsegood, M. R. J.; Smith, M. B.; Sanchez-Ballester, N. M. Dichloro( $\eta$ 6-p-cymene)(triphenylphosphine)ruthenium(II). Acta Crystallogr., Sect. E: Struct. Rep. Online **2006**, 62, m2838–m2840.

(16) (a) Krafft, M. E.; Wilson, L. J.; Onan, K. D. Synthesis and Characterization of Rhodium(I) Amino-Olefin Complexes. *Organo-metallics* **1988**, *7*, 2528–2534. (b) McCleverty, J.; Wilkinson, G.; et al. Dichlorotetracarbonyldirhodium (rhodium carbonyl chloride). *Inorg. Synth.* **2007**, *8*, 211–214.

(17) Tsang, D. S.; Yang, S.; Alphonse, F.-A.; Yudin, A. K. Stereoselective isomerization of N-allyl aziridines into geometrically stable Z enamines by using rhodium hydride catalysis. *Chem. - Eur. J.* **2008**, *14*, 886–894.

(18) (a) Ceriotti, A.; Ciani, G.; Sironi, A. The crystal and molecular structure of trans-chlorocarbonylbis(triphenylphosphine)rhodium(I) in its monoclinic form. *J. Organomet. Chem.* **1983**, 247, 345–350. (b) Boyd, S. E.; Field, L. D.; Hambley, T. W.; Partridge, M. G. Synthesis and characterization of Rh[P(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>(CO)CH<sub>3</sub> and Rh[P(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>(CO)Ph. *Organometallics* **1993**, *12*, 1720–1724.

(19) White, C.; Yates, A.; Maitlis, P. M.; Heinekey, D. M. ( $\eta^{5}$ -Pentamethylcyclopentadienyl)rhodium and -iridium compounds. *Inorg. Synth.* **2007**, *29*, 228–234.

(20) Snelders, D. J. M.; Siegler, M. A.; von Chrzanowski, L. S.; Spek, A. L.; van Koten, G.; Klein Gebbink, R. J. M. Coulombic inter-ligand repulsion effects on the Pt(II) coordination chemistry of oligocationic, ammonium-functionalized triarylphosphines. *Dalton Trans.* **2011**, *40*, 2588–2600.

(21) (a) Alt, H. G.; Baumgartner, R.; Brune, H. A. Über die Konfigurations- und Substituenten-Abhängigkeit der Pt-Cl-Valenzschwingungsfrequenzen und der <sup>31</sup>P-NMR-Parameter in substituierten *cis*- und *trans*-Dichlorobis(triphenylphosphan)platin(II)-Verbindungen. *Chem. Ber.* **1986**, *119*, 1694–1703. (b) Grim, S. O.; Keiter, R. L.; McFarlane, W. A Phosphorus-31 Nuclear Magnetic Resonance Study of Tertiary Phosphine Complexes of Platinum(II). *Inorg. Chem.* **1967**, *6*, 1133–1137. (c) Rigamonti, L.; Manassero, C.; Rusconi, M.; Manassero, M.; Pasini, A. *cis* Influence in *trans*-Pt(PPh<sub>3</sub>)<sub>2</sub> complexes. *Dalton Trans.* **2009**, 1206–1213.

(22) (a) Hammett, L. P. Effect of structure upon the reactions of organic compounds. Benzene derivatives. J. Am. Chem. Soc. 1937, 59, 96–103. (b) Keenan, S. L.; Peterson, K. P.; Peterson, K.; Jacobson, K. Determination of Hammett Equation Rho Constant for the Hydrolysis of p-Nitrophenyl Benzoate Esters. J. Chem. Educ. 2008, 85, 558–560.

(23) Clarke, M. L.; Ellis, D.; Mason, K. L.; Orpen, A. G.; Pringle, P. G.; Wingad, R. L.; Zaher, D. A.; Baker, R. T. The electron-poor phosphines  $P\{C_6H_3(CF_3)_2$ -3,5}3 and  $P(C_6F_5)_3$  do not mimic phosphites as ligands for hydroformylation. A comparison of the coordination chemistry of  $P\{C_6H_3(CF_3)_2$ -3,5}<sub>3</sub> and  $P(C_6F_5)_3$  and the unexpectedly low hydroformylation activity of their rhodium complexes. *Dalton Trans.* **2005**, 1294–1300.

(24) Cobley, C. J.; Pringle, P. G. Probing the bonding of phosphines and phosphites to platinum by NMR. Correlations of  ${}^{1}J(PtP)$  and Hammett substituent constants for phosphites and phosphines coordinated to platinum(II) and platinum (0). *Inorg. Chim. Acta* **1997**, 265, 107–115.

(25) Docherty, J. B.; Rycroft, D. S.; Sharp, D. W. A.; Webb, G. A. Restricted Rotation and Preferred Conformations in Tris-(pentafluorophenyl)phosphine Platinum(II) Complexes; the Mechanism of Helicity Reversal in a Co-ordinated Triarylphosphine. J. Chem. Soc., Chem. Commun. 1979, 336–337.

(26) (a) Pandey, M. K.; Mague, J. T.; Balakrishna, M. S. Sterically Demanding Phosphines with 2,6-Dibenzhydryl-4-methylphenyl Core: Synthesis of Ru<sup>II</sup>, Pd<sup>II</sup>, and Pt<sup>II</sup> Complexes, and Structural and Catalytic Studies. *Inorg. Chem.* **2018**, *57*, 7468–7480. (b) Bedford, R. B.; Hazelwood, S. L.; Albisson, D. A. Platinum Catalysts for Suzuki Biaryl Coupling Reactions. *Organometallics* **2002**, *21*, 2599–2600.

(27) Ahmad, N.; Ainscough, E. W.; James, T. A.; Robinson, S. D. Transition-metal Complexes Containing Phosphorus Ligands. Part IX. Triaryl Phosphite Derivatives of Palladium(II) and Platinum(II) Dihalides. J. Chem. Soc., Dalton Trans. **1973**, 1148–1150.

(28) Snelders, D. J. M.; Kunna, K.; Müller, C.; Vogt, D.; van Koten, G.; Klein Gebbink, R. J. M. Rh(I) coordination chemistry of hexacationic Dendriphos ligands and their application in hydroformylation catalysis. Tetrahedron: Asymmetry 2010, 21, 1411-1420. (29) (a) Serron, S.; Nolan, S. P.; Moloy, K. G. Solution Thermochemical Study of Tertiary Phosphine Ligand Substitution Reactions in the RhCl(CO)(PR<sub>3</sub>)<sub>2</sub> System. Organometallics 1996, 15, 4301-4306. (b) Egglestone, D. L.; Baird, M. C.; Lock, C. J. L.; Turner, G. Structures of Square-pyramidal Acyl and Octahedral Alkyl Intermediates in the Decarbonylation of Acid Halides by Chlorotris-(triphenylphosphine)rhodium(I). J. Chem. Soc., Dalton Trans. 1977, 1576-1582. (c) Oro, L. A.; Heras, J. V. Preparation and Reactions of Five-coordinate Rh(NBD)[P(p-Cl-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>]<sub>2</sub>X Complexes. Inorg. Chim. Acta 1979, 32, L37-L38. (d) Otto, S.; Roodt, A. Quantifying the electronic cis effect of phosphine, arsine and stibine ligands by use of rhodium(I) Vaska-type complexes. Inorg. Chim. Acta 2004, 357, 1-10. (e) Strohmeier, W.; Rehder-Stirnweiss, W. Änderung der Elektronendichte am Zentralatom des Katalysators RhX(CO)L<sub>2</sub> durch die Liganden X und L. Z. Naturforsch., B: J. Chem. Sci. 1970, 25b, 549-550. (f) Wang, K.; Goldman, M. E.; Emge, T. J.; Goldman, A. S. Transfer-dehydrogenation of alkanes catalyzed by rhodium(I) phosphine complexes. J. Organomet. Chem. 1996, 518, 55-68.

(30) Korenaga, T.; Ko, A.; Uotani, K.; Tanaka, Y.; Sakai, T. Angew. Chem., Int. Ed. **2011**, 50, 10703–10707.

(31) Assefa, M. K.; Devera, J. L.; Brathwaite, A. D.; Mosley, J. D.; Duncan, M. A. Vibrational scaling factors for transition metal carbonyls. *Chem. Phys. Lett.* **2015**, *640*, 175–179.

(32) (a) Schaarschmidt, D.; Kuhnert, J.; Tripke, S.; Alt, H. G.; Gorl, C.; Ruffer, T.; Ecorchard, P.; Walfort, B.; Lang, H. Ferrocenyl phosphane nickel carbonyls: Synthesis, solid state structure, and their use as catalysts in the oligomerization of ethylene. *J. Organomet. Chem.* **2010**, 695, 1541–1549. (b) Buchgraber, P.; Mercier, A.; Yeo, W. C.; Besnard, C.; Kündig, E. P. Functionalization of Planar Chiral Fused Arene Ruthenium Complexes: Synthesis, X-ray Structures, and Spectroscopic Characterization of Monodentate Triarylphosphines. *Organometallics* **2011**, *30*, 6303–6315.

(33) Carriedo, G. A.; Crochet, P.; Alonso, F. J. G.; Gimeno, J.; Presa-Soto, A. *Eur. J. Inorg. Chem.* **2004**, 3668–3674.

(34) Menéndez-Rodríguez, L.; Crochet, P.; Cadierno, V. Curr. Green Chem. 2013, 1, 128–135.