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Synthesis of Backbone *P*-Functionalized Imidazol-2-ylidene Complexes: *En Route* to Novel Functional Ionic Liquids

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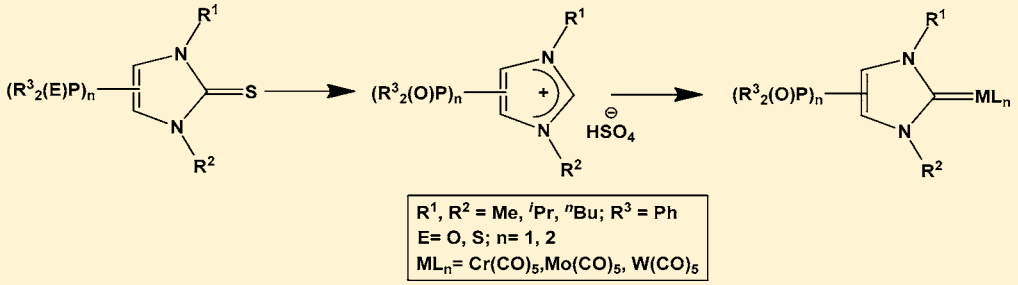
Supporting Information



ABSTRACT: 1-Alkyl-3-methyl-4-diphenylphosphoryl-imidazolium hydrogensulfate (**4a,b**) (**a**: $R^1 = R^2 = Me$; **b**: $R^1 = {}^iPr$, $R^2 = Me$) and 1-alkyl-3-methyl-4,5-bis(diphenylphosphoryl)imidazolium hydrogensulfate (**6a,c**) (**c**: $R^1 = {}^nBu$, $R^2 = Me$) were obtained selectively and in good yields by oxidative desulfurization of 1-alkyl-3-methyl-4-diphenylphosphino-imidazole-2-thiones (**2a,b**) and 1-*n*-butyl-3-methyl-4,5-bis(diphenylphosphoryl)imidazole-2-thione (**3c**) or 1,3-dimethyl-4-diphenylthiophosphoryl-5-diphenylphosphino-imidazole-2-thione (**5a**), respectively, with hydrogen peroxide. Synthesis of phosphoryl functionalized imidazol-2-ylidene complexes of group VI metal pentacarbonyls (**7a−9a**) and (**10b−12b**) and bis(phosphoryl) functionalized imidazol-2-ylidene complexes of group VI metal pentacarbonyls (**13c−15c**) and (**16a**) with low steric demand (methyl, isopropyl, *n*-butyl) at both *N*-centers was achieved through deprotonation of imidazolium salts (**4a,b**) and (**6a,c**), respectively,—having HSO_4^- as a counterion—with potassium *tert*-butoxide followed by rapid addition of metal pentacarbonyl acetonitrile complexes $[M(CO)_5(CH_3CN)]$ (M = Cr, Mo, W). The products were unambiguously characterized by elemental analyses, spectroscopic and spectrometric methods, and in addition, by single-crystal X-ray structure studies in the cases of **4b**, **8a**, **15c**, and **16a**; the latter two reveal imidazole ring bond distance alternation in contrast to **8a**.

INTRODUCTION

Since the discovery of "bottleable" 1,3-diadamantyl imidazol-2-ylidene, a representative of nowadays so-called N-heterocyclic carbenes (NHC's),[1] carbene chemistry has received enormous attention in coordination chemistry,[2] stabilization of highly reactive main group molecules,[3] homogeneous catalysis,[4] and beyond.[5] So far most of the frequently employed (unsaturated) imidazol-2-ylidene typically form metal complexes via the carbene carbon (C^2 position), while the C^4 and C^5 positions remain unsubstituted or bear only alkyl and/or aryl groups[6] (the numbering of elements in the imidazole ring follows the IUPAC recommendation[7]). However, there are few examples of imidazol-2-ylidenes that possess heteroatoms[8a−d] in the backbone. Functionalization of the imidazole 4- and/or 5-positions has been accomplished by a strategy that employs the lithiation of a 2-substituted imidazole (2-chloro or 2-thiono) followed by reaction with carbonyl electrophiles.[9] More recently, introduction of an additional donor atom(s) onto an imidazol-2-ylidene has been a subject of increased attention,[10−14] and functional groups such as amino,[10] hydroxy,[11] and phosphanyl[12] are representative of heteroatoms introduced *at the N-centers*. Phosphoranyl[15] and stiboranide[16] groups were first introduced into the 2-position of imidazol-2-ylidene by Schmutzler and Arduengo. However, additional donors *in the backbone* of imidazol-2-ylidene such as a phosphanyl group received less attention until Gates[13] and Bertrand[14] reported the first examples of C^4−phosphanyl substituted NHC's. While Gates exploited the inability to react at the C^2 center of imidazol-2-ylidenes bearing sterically demanding substituents at nitrogen center. Bertrand demonstrated the greater ease of rearrangement of a sterically demanding imidazol-2-ylidenes to the so-called abnormal adducts (coordination center in the backbone). Migrations of a C^2-bonded substituent to a C^4 (or C^5) site delivered 4- and 4,5-functionalized imidazol-2-ylidenes from a single 4,5-unsubstituted imidazol-2-ylidene. These bifunctional ligands proved to be useful in the synthesis of homo- and heterobimetallic complexes.[13,17] More recently,

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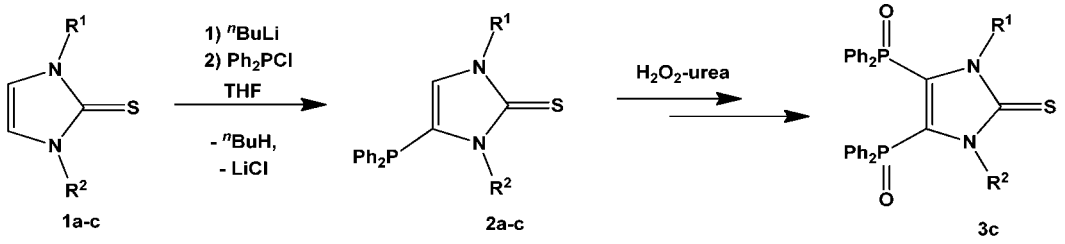
Scheme 1. Synthesis of *C*-Phosphanyl and/or *C*-Phosphoryl Substituted Imidazole-2-thiones 2a−c and 3c



Ruiz showed that rearrangement of C^2-bonded phosphanyl groups to the backbone can be driven by lithiation of the 4- and/or 5-positions, thus giving access to backbone-functionalized imidazol-2-ylidenes.[18] This approach allows the synthesis of backbone *P*-functionalized imidazol-2-ylidenes and complexes thereof having robust, (i.e., insensitive toward strong bases) but not functional phosphanyl groups. A different approach was developed to construct this substitution pattern while preserving the flexibility of the substitution pattern at both *N*-centers and in the backbone of the target imidazol-2-ylidenes. This approach takes advantage of the earlier developed lithiation strategies used for cyclopentadienyl-fused imidazole[9] and recently extended to phosphorus electrophiles.[19,36] Kuhn,[20] Wanzlick[21] (and Arduengo[22]) have already established methods for transformation of imidazole-2-thiones into imidazole-2-ylidenes. Furthermore, oxidative desulfurization methods of imidazole-2-thiones to get imidazolium salts are readily available using hydrogen peroxide and an acid,[22−25] benzoyl peroxide and sodium bicarbonate,[26] iron(III) chloride,[27] and nitric acid.[28−30] Robinson[31a,b] and Curran,[31c] also employed the backbone lithiation procedure for the C^4 functionalization of imidazol-2-ylidene-borane complexes. Although the strong σ-electron donor ability of imidazol-2-ylidenes has been used to great advantage to stabilize metal centers in high[32] and oxidation states,[33,34] the current goal is the fine-tuning of imidazol-2-ylidene properties *via* backbone-functionalization, hence providing flexibility to metal catalysts. Imidazol-2-ylidene group VI metal carbonyl complexes[33] are useful carbene transfer reagents to metals such as Pd, Pt, Rh, and Au.[35] Furthermore, 4,5-dichloro-imidazol-2-ylidenes[8d] (and complexes thereof) have revealed a remarkable stability toward moist air. A flexible synthetic approach to these systems will enable the study of phosphoryl modified imidazole-2-ylidenes and their metal complexes.

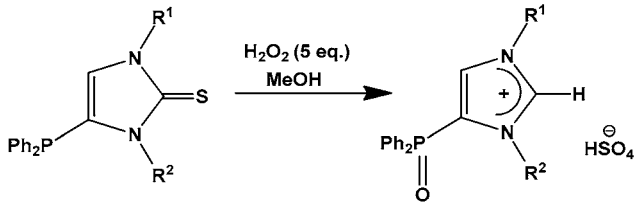
Herein, a convenient synthetic protocol for *P*-functional imidazolium salts (**4a,b** and **6a,c**) and their group VI (Cr, Mo, W) metal pentacarbonyl complexes (**7a−9a**, **10b−12b**, **13c−15c**, and **16a**) starting from *P*-functional imidazole-2-thiones (**2a,b**, **3c**, and **5a**) is reported.

RESULTS AND DISCUSSION

Recently, a simple access to mono- and bis(phosphoryl) substituted imidazole-2-thiones was reported.[19,36] Considering the convenient and high yield synthesis of 1,3-dialkyl-4-diphenylphosphino-imidazole-2-thiones[19] and 1-alkyl-3-methyl-4,5-bis(diphenylphosphoryl)imidazole-2-thione,[36] interest arose to explore the possibilities of generating *P*-functionalized imidazolium salts, thus studying their physical properties as well as reactivities, in particular with the interest to synthesize imidazol-2-ylidenes and complexes thereof. The imidazole-2-thione derivatives **1a−c**[37] were employed to construct 1,3-dialkyl-4-diphenylphosphino-imidazole-2-thiones **2a−c** *via* a lithiation/phosphanylation protocol (for the substituents used and respective numbering, see Scheme 1).[19,36] In order to enable comparison between a mono- and disubstituted derivative, **2c** was transformed into **3c** *via* an oxidation/phosphanylation/oxidation reaction sequence.[36]

Subsequently, **2a,b** and **3c** were treated with 5 and 4 equivalents of H_2O_2, respectively, in methanolic solution to give **4a,b** and **6c** through oxidative desulfurization (Scheme 2 and

Scheme 2. Oxidative Desulfurization of *P*-Functionalized Imidazole-2-thiones 2a,b



3). Treatment of **2a,b** with H_2O_2 led to a selective oxidation to give **4a,b**; the oxidation from a *P*(III) to a *P*(V) environment was distinctly reflected by downfield-shift of the ^{31}P resonances (compared to compounds **2a,b**). The bis(phosphoryl) substituted derivative **3c** could be converted directly into the corresponding imidazolium salt **6c** with the treatment of 4 equivalents of H_2O_2. Because the synthesis of **3a** (analogs of **3c**, R^1, R^2 = Me) were not obtained selectively and to access **6a** (analogous to **6c**, R^1, R^2 = Me), another synthetic protocol was developed. Treatment of **5a** (synthesis of **5a** is previously described[36]) with 6 equivalents of H_2O_2 (Scheme 3) resulted in the desulfurization of **5a** along with the (anticipated) oxidation of *P*(III) to *P*(V) as well as the interconversion of the thiophosphoryl into a phosphoryl group to give **6a**.

The resulting hygroscopic *P*-functional imidazolium hydrogensulfate **4a,b** and **6a,c** display resonances in the ^{31}P NMR spectra (methanolic solution) in a narrow chemical shift range of 15−17 ppm possessing a phosphorus−proton coupling constant ($^3J_{P,H}$) within the range of 9−12 Hz. As with the precursor **3c**, no coupling was observed between the two magnetically (and chemically) inequivalent phosphorus atoms in the backbone of the unsymmetrically substituted imidazolium hydrogensulfate **6c**, though they appear as two distinguishable signals in the ^{31}P NMR spectrum. The desulfurizations

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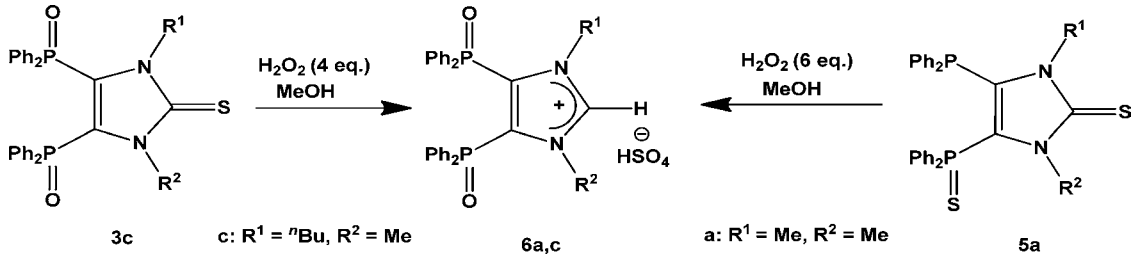
Scheme 3. Oxidative Desulfurization of *P*-Functionalized Imidazole-2-thiones 3c and 5a



and, hence, formation of imidazolium derivatives were firmly established through the ^{1}H NMR spectra, which revealed the C^2-proton in the range of 9.0−9.81 ppm. Further confirmation came through the ^{13}C NMR spectra showing the C^2-carbon resonance in the range of 140.0−146.0 ppm, while the (typical) thione carbon resonance (C^2) had disappeared. It should be noted that the observed NMR chemical shifts are strongly dependent on the solvent. The formations of **4a,b** and **6a,c** were independently confirmed by positive ESI mass spectrometry showing *m*/*z* values: 297.1 $[C_{17}H_{18}N_2OP]^+$ for **4a**, 325.15 $[C_{19}H_{22}N_2OP]^+$ for **4b**, 497.1 $[C_{29}H_{27}N_2O_2P_2]^+$ for **6a**, and 539.2 $[C_{32}H_{33}N_2O_2P_2]^+$ for **6c**.

Although desulfurizations of thiazoline-2-thiones[38] and imidazole-2-thiones[25,26,39] with H_2O_2 to give, respectively, thiazolium hydrogensulfates and imidazolium hydrogensulfates are known, the structure of an imidazolium hydrogensulfate has not previously been reported. Single-crystal X-ray diffraction study was performed for compound **4b** using a crystal obtained from a saturated ethanolic solution at low temperature (−20 °C). The compound **4b** crystallizes monoclinic in the space group *P*21/*c* (for crystallographic data, see Table S1 of the Supporting Information). The structure of **4b** is shown in Figure 1 together with selected structural parameters. Interatom distances and bond angles were found to be in the common range for imidazolium salts[40a] and *P*-oxide derivatives of imidazoles.[40b,c]

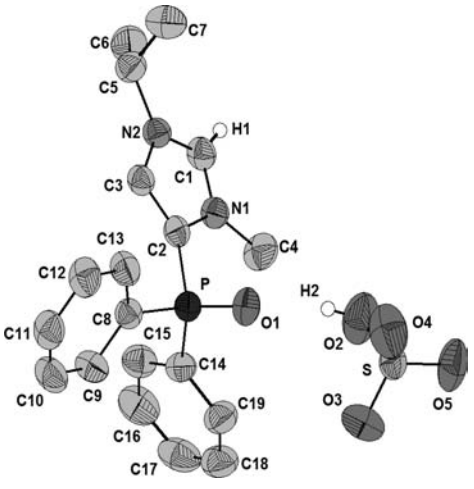


Figure 1. Molecular structure of compound **4b**. Hydrogen atoms (except H(1) (C^2−H) and H(2) (HSO_4^-)) have been omitted for clarity (50% probability level). Selected bond lengths (Å) and angles (deg) for compound **4b**: C(1)−N(1) 1.321(4), C(1)−N(2) 1.320(4), C(2)−C(3) 1.355(4), P(1)−O(1) 1.484(2), P(1)−C(2) 1.799(3), N(2)−C(1)−N(1) 109.4(2), O(1)−P-C(8) 112.25(12), C(14)−P-C(2) 104.99(12).

The structure of the imidazolium hydrogensulfate **4b** reveals an interesting role for the hydrogensulfate anion. Each hydrogensulfate anion experiences contacts with six nearest neighbor imidazolium ions out to a distance of about 3 Å. The closest interaction involves the hydrogensulfate anion acting as a hydrogen-bond donor to the oxygen of the phosphoryl moiety (r_{HO} = 0.82 and 1.87 Å; θ O−H−O = 162.7°). An electrostatic interaction appears to position the sulfur center of the hydrogensulfate anion about 4 Å above the plane of an imidazolium cation to which one oxo-group of the hydrogensulfate is positioned 3.08 Å above the formally cationic 2-position of the imidazolium ion. This latter oxo group also experiences a C−H-----O hydrogen bond to an isopropyl methine proton of another cationic unit (2.37 Å). The remaining interactions are also weak C−H-----O hydrogens bonds to hydrogens in the ortho-, meta-, and para-positions of phenyl groups, a methyl, and a C-4 imidazole hydrogen neighboring the hydrogensulfate anion (2.37−3.10 Å).[41]

The convenient availability of imidazolium hydrogensulfate **4a,b** and **6a,c** and ease of handling suggested that direct conversion of these salts into *P*-functional imidazol-2-ylidene complexes should be explored. The synthesis of imidazol-2-ylidene pentacarbonyl complexes of group (VI) metals using $M(CO)_6$[33] or photochemically[42] generated $[M(CO)_5(thf)]$ complexes or carbonyl metalates[43] with either free or *in situ* generated imidazol-2-ylidenes have been reported, but the additional acidic proton on the hydrogensulfate counterion has been a source of problems in the generation of some imidazol-2-ylidenes.[22]

Nonetheless, in these cases deprotonation of the *P*-functionalized imidazolium salts (**4a,b** and **6a,c**) and *in situ* complexation with $[M(CO)_5(CH_3CN)]$[44] (M = Cr−W) could be accomplished by using one mole-equivalent of potassium *tert*-butoxide in THF at 60 °C, greatly shortening the time required for the synthetic protocol by eliminating the need for an anion exchange. All complexes were purified by washing with diethyl ether/*n*-pentane. The constitution of the *P*-functional imidazol-2-ylidene complexes **7a−9a**, **10b−12b** (from **4a,b**) (Scheme 4), and **13c−15c**, **16a** (from **6a,c**) (Scheme 5) was confirmed by various spectroscopic and spectrometric methods.

The ^{13}C NMR chemical shifts are listed in Table 1. One phosphoryl group causes a downfield-shift of the carbene carbon atom resonance by about 10 ppm, whereas two phosphoryl groups causes downfield shifts of about 16 ppm relative to the C^4- and C^5-unsubstituted imidazol-2-ylidene (VI) metal carbonyl complexes of type **A** (shown in Table 1) reported by Öfele[33(a)] and co-workers; this trend was observed for all complexes of all three metals (Cr, Mo, W). This chemical shift trend may be the result of a slight twisting of the imidazole ring by the bulky phosphoryl substituents and a slight negative

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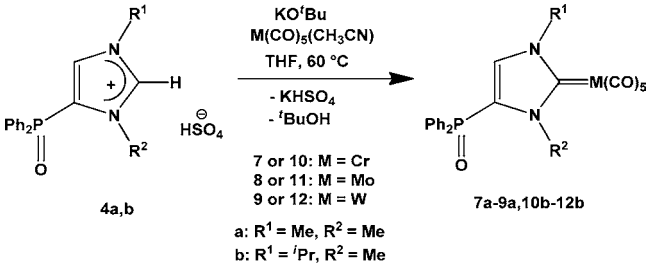
Scheme 4. Synthesis of *P*-Functional Imidazol-2-ylidene Complexes of Group VI Metals 7a−9a and 10b−12b



Scheme 5. Synthesis of *C*-Bis(phosphoryl) Backbone-Substituted Imidazol-2-ylidene Complexes of Group VI Metals 13c−15c and 16a

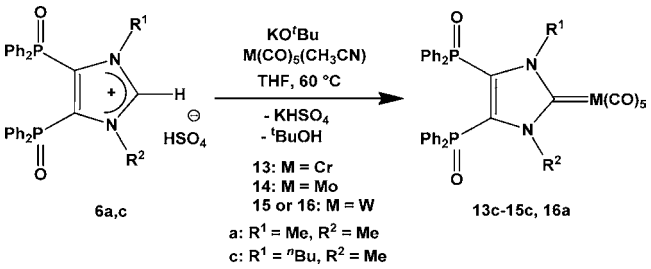
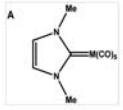
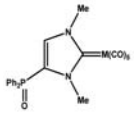
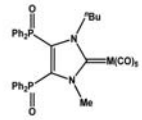


Table 1. Comparison of ^{13}C NMR Chemical Shifts [ppm] of C^2 Nuclei and Carbonyl Stretching Vibrations of the A$_1$ Mode [cm^{-1}] in IR Spectra with Literature Known Derivatives of Type A[33a]

^{13}C NMR chemical shifts [ppm] of C^2 nuclei			
M			
Cr	188.3	199.8	204.5
Mo	186.5	196.4	199.9
W	178.5	187.9	190.1
A$_1$ carbonyl stretching modes [cm^{-1}]			
Cr	2056	2057	2065
Mo	2064	2067	2064
W	2062	2064	2063

hyperconjugation that reduces the cyclic delocalization within the imidazole ring and enhances a paramagnetic contribution to the chemical shift tensor at the carbene carbon atom.

The IR spectroscopic and mass spectrometric data of **7a−9a**, **10b−11b**, and **13c−15c** are given in the Experimental Section. All complexes displayed three carbonyl stretching bands in the IR spectra in the range of 2067−2055, 1982−1965, and 1929−1876 [cm^{-1}] depending upon the substituents at the nitrogen atoms and metal used. As seen from Table 1, there is a significant effect of the phosphoryl group(s) on the C^2 resonances (and trend), while there is one on the A$_1$ stretching mode exclusively for the Cr(CO)$_5$ moiety, whereas absorptions due to the Mo(CO)$_5$ and the W(CO)$_5$ vibrations are invariant compared to reported compounds.[33a] In EI-MS experiments, the loss of one (or more) CO molecule(s) from the molecule radical cations was the preferred mode of fragmentation for all imidazol-2-ylidene complexes, but a loss of the imidazol-2-ylidene ligand as well as a phosphoryl group was also observed in some cases (**8a**, **10b**, **11b**, and **14c**).

Single-crystal X-ray diffraction studies were also performed for complexes **8a**, **15c**, and **16a.** Crystals were obtained from saturated diethylether solutions at low temperature (−20 °C). For crystallographic data see Table S1 and Table S2 of the Supporting Information. The selected structural parameters are given in Table 2, and the molecular structures of **8a**, **15c**, and **16a** are shown in Figures 2, 3 and 4, respectively, and provide constitutional proof. The unit cell of **15c** contains one solvent (diethylether) molecule. Because there is no interaction of the diethylether with the molecule of interest, we have omitted the diethylether in Figure 3 for clarity. All three compounds **8a**, **15c**, and **16a** contain metal atoms (molybdenum or tungsten) having a slightly distorted octahedral geometry. The N(1)−C(1)−Mo angle in **8a** (129.7(3)°) is slightly larger than N(2)−C(1)−Mo angle (126.8(2)°), which is probably caused by the phosphoryl group at C^4 position. Similar observations were reported for other dissymmetrically substituted imidazol-2-ylidene complexes.[45] The Mo−C bonds to the *cis*-CO groups are slightly elongated compared to the Mo−C bond to the *trans*-CO. The Mo−C(1) bond (to the carbene carbon atom) is 2.264(4) Å, which compares well with the reported data for a tris(carbene) complex of the type *fac*-Mo(CO)$_3$(I)$_3$.[33c] The W−C(1) bond lengths in **15c** (2.268(4)) Å and **16a** (2.282(10) Å are well comparable to corresponding parameters in tungsten complexes with benz-annulated *N*-heterocyclic

Table 2. Selected Atom Distances (Å) and Bond Angles (deg) for Compounds 8a, 15c, and 16a

8a		15c		16a	
C(1)−Mo	2.264(4)	C(1)−W	2.268(4)	C(1)−W(1)	2.282(10)
C(18)−Mo	1.985(4)	C(33)−W	1.985(4)	C(30)−W(1)	1.984(12)
C(22)−Mo	2.075(4)	C(36)−W	2.036(4)	C(34)−W(1)	2.032(11)
O(1)−P	1.484(3)	P(2)−O(2)	1.483(2)	P(2)−O(2)	1.466(7)
C(2)−P	1.789(3)	C(3)−P(2)	1.828(4)	C(2)−P(1)	1.836(9)
C(1)−N(1)	1.371(4)	C(1)−N(1)	1.366(4)	C(1)−N(1)	1.340(12)
C(1)−N(2)	1.381(5)	C(1)−N(2)	1.373(4)	C(1)−N(2)	1.357(13)
N(1)−C(2)	1.398(4)	N(1)−C(2)	1.400(4)	N(1)−C(2)	1.404(13)
C(2)−C(3)	1.360(5)	C(2)−C(3)	1.378(4)	C(2)−C(3)	1.376(13)
C(3)−N(2)	1.371(4)	C(3)−N(2)	1.383(4)	C(3)−N(2)	1.415(13)
N(1)−C(1)−Mo	129.7(3)	N(1)−C(1)−W	129.6(2)	N(1)−C(1)−W(1)	127.8(7)
N(2)−C(1)−Mo	126.8(2)	N(2)−C(1)−W	127.5(2)	N(2)−C(1)−W(1)	127.3(7)
C(2)−P−C(11)	100.47(17)	C(3)−P(2)−C(31)	109.95(15)	C(2)−P(1)−C(12)	105.1(5)
N(1)−C(1)−N(2)	102.7(3)	N(1)−C(1)−N(2)	102.7(3)	N(1)−C(1)−N(2)	104.7(8)

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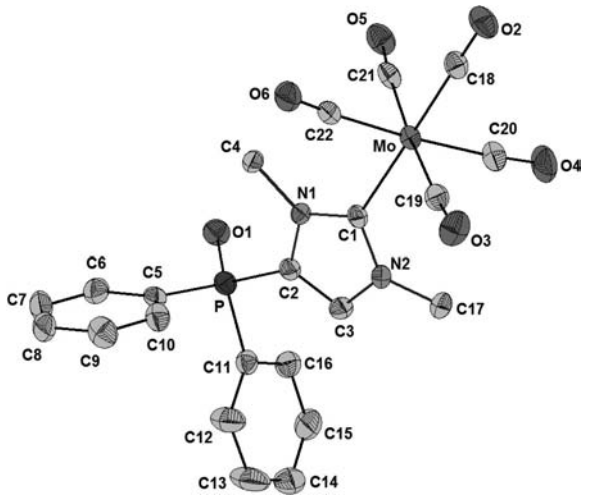

Figure 2. Molecular structure of complex **8a.** Hydrogen atoms have been omitted for clarity (50% probability level).

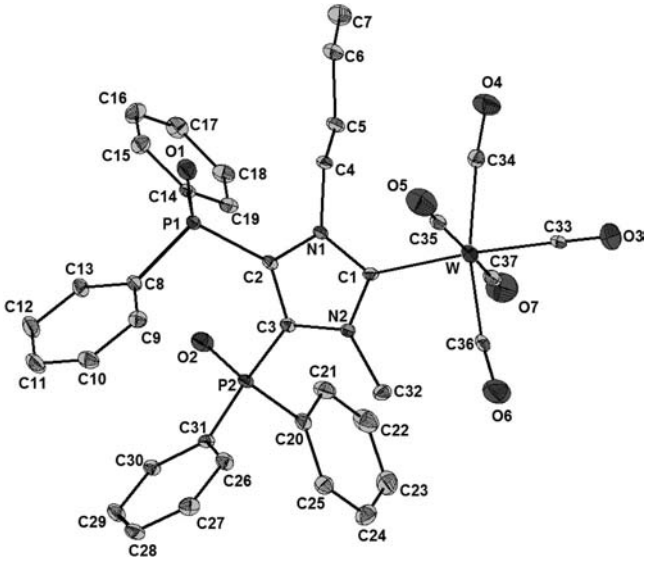

Figure 3. Molecular structure of compound **15c.** Hydrogen atoms have been omitted for clarity (30% probability level).

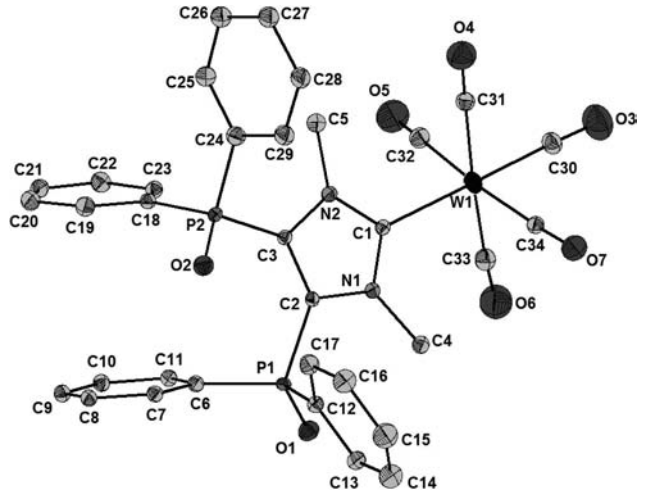

Figure 4. Molecular structure of compound **16a.** Hydrogen atoms have been omitted for clarity (30% probability level).

carbene ligands.[46,47] An interesting feature is the contrast between the ring atom distances in the imidazole^{Me,Me} ligands of **8a** and **16a** as there is strict bond alternation in **16a** whereas **8a** displays well-balanced bond lengths as typical structural signature for a degree of delocalization in imidazole-2-ylidenes (however, the σ-effects in these systems need to be considered as well). Noteworthy is that atoms P(1) and P(2) for **15c** are found slightly out of the plane of the imidazole-2-thione ring: the dihedral angles of the P(1)−C(2)−C(3) plane and the best imidazole plane is 8.60°, and the P(2)−C(3)−C(2) plane and the imidazole plane is 13.19°. The torsion angle between P(1)−C(2)−C(3) plane and P(2)−C(3)−C(2) plane is 21.77°. Furthermore, two different dihedral angles were found for the O−P−C units and the imidazole-2-thione ring plane: 26.74° for the O(1)−P(1)−C(2) plane and 25.13° for the O(2)−P(2)−C(3) plane. The PO units are located on opposite sides of the imidazole-2-thione plane.

As observed for **15c**, the P−C bond length is elongated in **16a** (C(2)−P(1) 1.836(9) Å) compared to **8a** (C(2)−P(1) 1.789(3) Å), and atoms P(1) and P(2) in compound **16a** (and **15c**) are slightly out of the plane of the imidazole-2-thione ring: the dihedral angles of the P(1)−C(2)−C(3) plane and the imidazole best plane is 9.02°, and the P(2)−C(3)−C(2) plane and the imidazole plane is 12.36°. The torsion angle between P(1)−C(2)−C(3) plane and P(2)−C(3)−C(2) plane is 21.36°. Again two different dihedral angles were found for the O−P−C units and the imidazole-2-thione ring plane: 33.79° for the O(1)−P(1)−C(2) plane and 39.92° for the O(2)−P(2)−C(3) plane. Thus, the PO units are located on opposite sides of the imidazole-2-thione plane similar to the situation described for **15c**.

CONCLUSIONS

A facile synthetic methodology was developed that allows access to mono- and bis(phosphoryl) backbone-functionalized imidazolium hydrogensulfate **4a,b** and **6a,c**. With melting points in the range of 60 to 120 °C, these compounds—especially **4a,b**—show a tendency to behave as ionic liquids and thus represent leading examples of Imz backbone P-functional ILs. Without exchanging the hydrogensulfate counterion, these imidazolium salts were subjected to a novel deprotonation/complexation protocol using the combination of potassium *tert*-butoxide and $[M(CO)_5(CH_3CN)]$ (M = Cr−W) and heating to 60 °C to yield a series of imidazol-2-ylidene carbonyl complexes of group VI metals **7a−9a**, **10b−12b**, and **13c−15c**, **16a**. The presence of one (or two) phosphoryl group(s) at the C^4 and/or C^5 position caused a downfield-shift of the carbene carbon atom resonance by ∼10 ppm (for C^4-substituted derivatives) and ∼16 ppm (for C^4- and C^5-substituted derivatives) compared to (known) backbone unsubstituted derivatives. The strong effect of two phosphoryl groups is also reflected in the structural data of **15c** and **16a** as the (more) typical NHC ligand present in **8a** is "tuned" into an unsaturated NHC ligand analog with strictly alternating ring bond distances. On-going studies are directed toward the synthesis of homo- and heterobimetallic complexes in which the complex unit(s) are an integral part of the cationic core of ionic ligands.

EXPERIMENTAL SECTION

General Considerations. The synthesis of the imidazol-2-ylidene complexes were performed under an argon atmosphere, using common Schlenk techniques and dry solvents. Tetrahydrofuran, diethyl ether, and *n*-pentane were dried over sodium wire/

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benzophenone and further purified by subsequent distillation. Complexes $[M(CO)_5(CH_3CN)]$ were prepared following the literature protocol.[44] All other chemicals were used as purchased. All NMR spectra were recorded on a Bruker AX-300 spectrometer (300.1 MHz for ^1H, 75.5 MHz for ^{13}C, 121.5 MHz for ^{31}P). The ^1H and ^{13}C NMR spectra were referenced to the residual proton resonances and the ^{13}C NMR signals of the deuterated solvents and ^{31}P to 85% H_3PO_4 as external standard, respectively. Melting points were determined in one-side melted off capillaries using a Büchi Type S or a Carl Roth Type MPM-2 apparatus; they are uncorrected. Elemental analyses were carried out on a Vario EL gas chromatograph. Mass spectrometric data were collected on a Kratos MS 50 spectrometer using EI, 70 eV. The infrared spectra were recorded on a Nicolet 80 FT-IR spectrometer using KBr pellets. The UV/vis spectra were recorded in solution on a Shimadzu UV-1950 PC spectrometer. The X-ray analyses were performed on a Nonius Kappa CCD or a Bruker X8-KappaApex TT type diffractometer at 123(2) or 100(2) K, respectively. The structures were solved by direct methods refined by full-matrix least-squares technique in anisotropic approximation for non-hydrogen atoms using SHELXS97 and SHELXL97[48] program packages. Hydrogen atoms were located from Fourier synthesis and refined isotropically. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-888222 (**4b**), CCDC- 888223 (**8a**), 888224 (**15c**), and CCDC- 888225 (**16a**), which can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

General Procedure for the Oxidative Desulfurization of *P*-Functionalized Imidazole-2-thiones 2a,b, 3c, and 5a. To a solution of **2a,b**, **3c**, or **5a** (10 mmol each) in 40 mL of methanol, 5, 4, or 6 equivalents of H_2O_2, respectively, was added at 0 °C. The reaction mixture was stirred at 0 °C for 30 min, then at r.t. for 45 min, and then concentrated *in vacuo* (8×10^{-3} mbar). The residual syrup-like liquids **4a,b** and **6a,c**, were crystallized from 10 mL of isopropanol at −20 °C.

1,3-Dimethyl-4-diphenylphosphorylimidazolium Hydrogensulfate (4a). Yield: 3.63 g (9.2 mmol, 92%), colorless solid, mp 80 °C. ^1H NMR (300 MHz, CD_3CN): δ = 3.83 (s, 3H, N^3-CH_3), 3.85 (s, 3H, N^1-CH_3), 7.22 (s br, 1H, C^5-H), 7.58−7.67 (m, 4H, C_6H_5-H), 7.70−7.81 (m, 6H, C_6H_5-H), 9.56 (s, 1H, C^2-H). $^{13}C\{^1H\}$ NMR (75.0 MHz, CD_3CN): δ = 35.6 (s, N^3-CH_3), 35.7 (s, N^1-CH_3), 127.1 (d, $^1J_{P,C}$ = 116.1 Hz, C^4), 129.0 (d, $J_{P,C}$ = 12.9 Hz, C_6H_5), 129.1 (d, $^1J_{P,C}$ = 113.1 Hz, *ipso*-C_6H_5), 131.2 (d, $J_{P,C}$ = 10.6 Hz, C_6H_5), 132.0 (d, $^2J_{P,C}$ = 18.7 Hz, C^5), 132.2 (d, $J_{P,C}$ = 3.0 Hz, C_6H_5), 142.0 (d, $J_{P,C}$ = 4.9 Hz, C^2). ^{31}P NMR (121.5 MHz, CD_3CN): δ = 16.2 (quint br, $^3J_{P,H}$ = 12.6 Hz). IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3140 and 3049 (w, ν(C−H)), 1438 (s), 1402 (s, ν(C−N)) and 1191 (s, ν(P═O)). UV/vis (CH_2Cl_2): λ_{max}: 228 nm. Pos. ESI-MS: $C_{17}H_{18}N_2OP^+$ calcd (found) 297.1 (297.1), neg. ESI-MS: HSO_4^- calcd (found) 97.0 (97.0). Due to the high hygroscopicity, no reliable elemental analysis could be obtained.

1-Isopropyl-3-methyl-4-diphenylphosphorylimidazolium Hydrogensulfate (4b). Yield: 3.71 g (8.8 mmol, 88%), colorless solid, mp 63 °C. ^1H NMR (300 MHz, D_2O): δ = 1.39 (d, $^3J_{H,H}$ = 6.8 Hz, 6H, $C_3H_7-CH_3$), 3.67 (s, 3H, N^3-CH_3), 4.49 (hept, $^3J_{H,H}$ = 6.7 Hz, 1H, C_3H_7-CH), 7.37 (br s, 1H, C^5-H), 7.70−7.48 (m, 10H, C_6H_5-H), 9.09 (s, 1H, C^2-H). $^{13}C\{^1H\}$ NMR (75.0 MHz, D_2O): δ = 21.7 (s, $C_3H_7-CH_3$), 35.9 (d, $^3J_{P,C}$ = 0.8 Hz, N^3-CH_3), 54.1 (s, C_3H_7-CH), 126.3 (d, $^1J_{P,C}$ = 115.5 Hz, *ipso*-C_6H_5), 126.5 (d, $^1J_{P,C}$ = 118.5 Hz, C^4), 129.6 (d, $J_{P,C}$ = 13.6 Hz, C_6H_5), 130.7 (d, $^2J_{P,C}$ = 20.0 Hz, C^5), 131.6 (d, $J_{P,C}$ = 11.3 Hz, C_6H_5), 134.4 (d, $J_{P,C}$ = 2.9 Hz, C_6H_5), 140.6 (d, $J_{P,C}$ = 5.3 Hz, C^2). ^{31}P NMR (121.5 MHz, D_2O): δ = 22.4 (quint br, $^3J_{P,H}$ = 12.0 Hz). IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3133 and 3031 (w, ν(C−H)), 1436 (s), 1396 (s) and 1232 (s, ν(P═O)). UV/vis (CH_2Cl_2): λ_{max}: 231 nm. Pos. ESI-MS: $C_{19}H_{22}N_2OP^+$ calcd (found) 325.15 (325.15), neg. ESI-MS: HSO_4^- calcd (found) 97.0 (97.0). Due to the high hygroscopicity, no reliable elemental analysis could be obtained.

1, 3-Dimethyl-4,5-bis(diphenylphosphoryl)imidazolium Hydrogensulfate (6a). Colorless solid. ^1H NMR (300 MHz, CD_3CN): δ = 3.65 (s, 6H, $N-CH_3$), 7.37−7.45 (m, 8H, C_6H_5-H), 7.54−7.66 (m, 12H, C_6H_5-H), 9.81 (s, 1H, C^2-H). $^{13}C\{^1H\}$ NMR (75.0 MHz, CD_3CN): δ= 37.5 (s, $N-CH_3$), 128.2 (d, $J_{P,C}$ =13.5 Hz, C_6H_5), 129.8 (dd, $^1J_{P,C}$ =116.7 Hz, *ipso*-C_6H_5), 131.8 (d, $J_{P,C}$ =11.3 Hz, C_6H_5), 132.8 (d, $J_{P,C}$ =2.9 Hz, C_6H_5), 135.3 (d, $^1J_{P,C}$ =116.7 Hz, $^2J_{P,C}$ =10.2 Hz, C^4/C^5), 146.0 (dd, $J_{P,C}$ = 5.4 Hz, C^2).^{31}P NMR (121.5 MHz, CD_3CN): δ = 23.7 (quint br, $^3J_{P,H}$ = 13.0 Hz). Pos.-ESI-MS: $C_{29}H_{27}N_2O_2P_2^+$ calcd (found) 497.1 (497.1), neg-ESI-MS: HSO_4^- calcd (found) 97.0 (97.0). **6a** was obtained with 90% purity according to the ^{31}P NMR spectrum (10% nonidentified impurities) and were used further for complexation reaction.

1-*n*-Butyl-3-methyl-4,5-bis(diphenylphosphoryl)-imidazolium Hydrogensulfate (6c). Yield: 5.6 g (8.8 mmol, 88%), colorless solid, mp 119 °C. ^1H NMR (300 MHz, D_2O): δ = 0.56 (t, $^3J_{H,H}$ =7.2 Hz, 3H, $C_4H_9-CH_3$), 0.87−1.00 (m, 2H, $C_4H_9-CH_2$), 1.41 (s br, 2H, $C_4H_9-CH_2$), 3.43 (s, 3H, N^3-CH_3), 4.10 (s br, 2H, $C_4H_9-CH_2$), 7.22−7.56 (m, 20H, C_6H_5-H), 9.32 (s, 1H, C^2-H). $^{13}C\{^1H\}$ NMR (75.0 MHz, D_2O): δ= 12.5 ($C_4H_9-CH_3$), 18.8 ($C_4H_9-CH_2$), 31.8 ($C_4H_9-CH_2$), 38.2 (N^3-CH_3), 51.1 ($C_4H_9-CH_2$), 127.6 (d, $^1J_{P,C}$ =116.0 Hz, *ipso*-C_6H_5), 127.8 (d, $^1J_{P,C}$ =116.7 Hz, *ipso*-C_6H_5), 128.9 (d, $J_{P,C}$ =13.7 Hz, C_6H_5), 129.1 (d, $J_{P,C}$ =13.6 Hz, C_6H_5), 131.7 (d, $J_{P,C}$ =11.5 Hz, C_6H_5), 132.0 (d, $J_{P,C}$ =11.3 Hz, C_6H_5), 134.1 (d, $J_{P,C}$ =2.9 Hz, C_6H_5), 134.6 (dd, $^1J_{P,C}$ =105.9 Hz, $^2J_{P,C}$ =15.8 Hz, C^4/C^5), 134.6 (dd, $^1J_{P,C}$ =105.7 Hz, $^2J_{P,C}$ =15.4 Hz, C^5/C^4), 145.3 (dd, $J_{P,C}$ = 5.5 Hz, C^2).^{31}P NMR (121.5 MHz, D_2O): δ = 29.4 (quint br, $^3J_{P,H}$ = 13.1 Hz), 27.6 (quint br, $^3J_{P,H}$ = 13.1 Hz). Pos. ESI-MS: $C_{32}H_{33}N_2O_2P_2^+$ calcd (found) 539.2 (539.2), neg. ESI-MS: HSO_4^- calcd (found) 97.0 (97.0). Due to the high hygroscopicity, no reliable elemental analysis could be obtained.

General Procedure for the Synthesis of Backbone *P*-Functional Imidazol-2-ylidene Complexes 7a−9a, 10b−12b, 13c−15c, 16a. To freshly prepared solutions of complexes $[MCO)_5(CH_3CN)]$ (M = Cr, Mo, W) (1.05 mmol each) in 8 mL of tetrahydrofuran, a solution containing the *P*-functional imidazolium hydrogensulfate (**4a,b** and **6a,c**) (1 mmol each) and potassium *tert*-butoxide (1.05 mmol) in 8 mL of tetrahydrofuran was added at ambient temperature. The reaction mixture was heated at 60 °C for 16 h. The formed potassium hydrogensulfate was separated by filtration over cannulae. The yellow-orange colored solutions were then concentrated *in vacuo* (8×10^{-3} mbar) followed by washing with *n*-pentane (2 × 5 mL) and then dried *in vacuo*.

[Pentacarbonyl(1,3-dimethyl-4-diphenylphosphoryl-imidazol-2-ylidene)chromium(0)] (7a). Yield: 0.39 g (0.81 mmol, 81%), yellow solid, mp 170 °C (dec.). ^1H NMR (300 MHz, $CDCl_3$): δ = 3.76 (s, 3H, N^3-CH_3), 3.82 (s, 3H, N^1-CH_3), 6.52 (d, $^3J_{P,H}$ = 1.8 Hz, 1H, C^5-H), 7.45−7.68 (m, 10H, C_6H_5-H). $^{13}C\{^1H\}$ NMR (75.0 MHz, $CDCl_3$): δ = 37.9 (d, $^3J_{P,C}$ = 1.4 Hz, N^3-CH_3), 38.5 (s, N^1-CH_3), 127.4 (d, $^1J_{P,C}$ = 120.8 Hz, C^4), 128.1 (d, $J_{P,C}$ = 12.8 Hz, C_6H_5), 129.2 (d, $^1J_{P,C}$ = 112.5 Hz, *ipso*-C_6H_5), 130.5 (d, $J_{P,C}$ = 10.6 Hz, C_6H_5), 132.0 (d, $J_{P,C}$ = 2.9 Hz, C_6H_5), 132.8 (d, $^2J_{P,C}$ = 21.7 Hz, C^5), 199.8 (s br, C^2), 216.3 (*cis*-CO), 220.1 (*trans*-CO. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 15.6 (quint br, $^3J_{P,H}$ = 12.3 Hz). IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3139 and 3089 (w, ν(C−H)), 2057 (s, ν(CO)), 1979(s, ν(CO)), 1878 (s, ν(CO)), 1436 (s) and 1292 (s, ν(P═O)).UV/vis (CH_2Cl_2): λ_{max}: 260 nm. MS (EI, 70 eV): *m*/*z* (%) 488 (14) $[M]^+$, 376 (22) $[M-4CO]^+$, 348 (100) $[M-5(CO)]^+$, 296 (38) $[M-Cr(CO)_5]^+$, 201 (60) $[C_{12}H_{10}OP]^+$. EA: calcd. for $C_{22}H_{17}CrN_2O_6P$: C 54.11, H 3.51, N 5.74 found: C 53.33, H 3.99, N 6.37.

[Pentacarbonyl(1,3-dimethyl-4-diphenylphosphoryl-imidazol-2-ylidene)molybdenum(0)] (8a). Yield: 0.39 g (0.74 mmol, 74%), yellow solid, mp 158 °C (dec.). ^1H NMR (300 MHz, $CDCl_3$): δ = 3.73 (s, 3H, N^3-CH_3), 3.80 (s, 3H, N^1-CH_3), 6.54 (br s, 1H, C^5-H), 7.44−7.69 (m, 10H, C_6H_5-H). $^{13}C\{^1H\}$ NMR (75.0 MHz, $CDCl_3$): δ = 38.5 (d, $^3J_{P,C}$ = 1.1 Hz, N^3-CH_3), 39.1 (s, N^1-CH_3), 126.0 (d, $^1J_{P,C}$ = 120.5 Hz, C^4), 128.0 (d, $J_{P,C}$ = 12.9 Hz, C_6H_5), 129.3 (d, $^1J_{P,C}$ = 112.2 Hz, *ipso*-C_6H_5), 130.5 (d, $J_{P,C}$ = 10.5 Hz, C_6H_5), 132.0 (d, $J_{P,C}$ = 2.9 Hz, C_6H_5), 132.1 (d, $^2J_{P,C}$ = 21.8 Hz, C^5), 196.4 (s br, C^2), 205.2 (*cis*-CO), 210.4 (*trans*-CO). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 15.5 (quint br, $^3J_{P,H}$ = 12.7 Hz). IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3128 and 3076 (w, ν(C−H)), 2067 (s, ν(CO)), 1981(s, ν(CO)), 1876 (s, ν(CO)), 1436 (s) and 1207 (s, ν(P═O)),753 and 723 (s, $\delta(C_6H_5)$). UV/vis (CH_2Cl_2): λ_{max}: 253 nm. MS (EI, 70 eV): *m*/*z* (%) 82 (100) $[C_4H_6N_2]^+$, 65 (86) $[C_3H_3N_2]^+$. EA: calcd. for

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$C_{22}H_{17}MoN_2O_6P$: C 49.64, H 3.22, N 5.26 found: C 47.33, H 3.75, N 5.70.

[Pentacarbonyl(1,3-dimethyl-4-diphenylphosphoryl-imidazol-2-ylidene)tungsten(0)] (9a). Yield: 0.45 g (0.72 mmol, 72%), yellow solid, mp 198 °C (dec.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.74 (s, 3H, N^3-CH_3), 3.80 (s, 3H, N^1-CH_3), 6.54 (d, $^3J_{P,H}$ = 1.9 Hz, 1H, C^5-H), 7.45−7.70 (m, 10H, C_6H_5-H). $^{13}C\{^1H\}$ NMR (75.0 MHz, $CDCl_3$): δ = 39.4 (d, $^3J_{P,C}$ = 1.1 Hz, N^3-CH_3), 40.0 (s, N^1-CH_3), 126.7 (d, $^1J_{P,C}$ = 120.2 Hz, C^4), 128.1 (d, $J_{P,C}$ = 12.6 Hz, C_6H_5), 129.2 (d, $^1J_{P,C}$ = 112.3 Hz, *ipso*-C_6H_5), 130.6 (d, $J_{P,C}$ = 10.5 Hz, C_6H_5), 131.7 (d, $^2J_{P,C}$ = 21.7 Hz, C^5), 132.1 (d, $J_{P,C}$ = 2.9 Hz, C_6H_5), 187.9 (d, $J_{P,C}$ = 1.0 Hz, C^2), 196.7 (s_{sat}, $^1J_{C,W}$ = 126.4 Hz, *cis*-CO), 199.5 (s_{sat}, $^1J_{C,W}$ = 132.1 Hz, *trans*-CO). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 15.6 (quint br, $^3J_{P,H}$ = 12.9 Hz). IR (KBr, cm^{-1}): $\tilde{\upsilon}$ = 3135 and 3096 (w, υ(C−H)), 2064 (s, υ(CO)), 1982(s, υ(CO)), 1884 (s, υ(CO)), 1436 (s) and 1232 (s, υ(P═O)) UV/vis (CH_2Cl_2): λ_{max}: 250 nm. MS (EI, 70 eV): *m*/*z* (%) 620 (36) $[M]^{\cdot+}$, 592 (40) $[M-CO]^+$, 590 (30) $[C_{20}H_{11}N_2O_6PW]^+$, 564 (40) $[M-2CO]^+$, 536 (20) $[M-3CO]^+$, 508 (20) $[M-4CO]^+$, 480 (92) $[M-5CO]^+$, 420 (22) $[C_{10}H_7N_2O_5W]^+$, 296 (22) $[M-W(CO)_5]^+$, 82 (100) $[C_4H_6N_2]^+$. EA: calcd. for $C_{22}H_{17}N_2O_6PW$: C 42.61, H 2.76, N 4.52 found: C 41.86, H 3.11, N 4.66.

[Pentacarbonyl(1-isopropyl-3-methyl-4-diphenylphosphoryl-imidazol-2-ylidene)chromium(0)] (10b). Yield: 0.41 g (0.8 mmol, 80%), yellow solid, mp 173 °C(dec.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.28 (d, $^3J_{H,H}$ = 6.5 Hz, 6H, $C_3H_7-CH_3$), 3.82 (s, 3H, N^3-CH_3), 5.16 (hept, $^3J_{H,H}$ = 6.5 Hz, 1H, C_3H_7-CH), 6.58 (br s, 1H, C^5-H), 7.45−7.70 (m, 10H, C_6H_5-H). $^{13}C\{^1H\}$ NMR (75.0 MHz, $CDCl_3$): δ = 22.7 (s, C_3H_7-CH_3), 37.7 (d, $^3J_{P,C}$ = 1.2 Hz, N^3-CH_3), 51.9 (s, C_3H_7-CH), 127.4 (d, $^2J_{P,C}$ = 21.9 Hz, C^5), 128.1 (d, $J_{P,C}$ = 12.8 Hz, C_6H_5), 128.4 (d, $^1J_{P,C}$ = 120.5 Hz, C^4), 129.3 (d, $^1J_{P,C}$ = 112.2 Hz, *ipso*-C_6H_5), 130.5 (d, $J_{P,C}$ = 10.4 Hz, C_6H_5), 132.0 (d, $J_{P,C}$ = 2.9 Hz, C_6H_5), 198.3 (s br, C^2), 216.5 (*cis*-CO), 220.3 (*trans*-CO). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 15.8 (quint br, $^3J_{P,H}$ = 12.4 Hz). IR (KBr, cm^{-1}): $\tilde{\upsilon}$ = 3109 and 3054 (w, υ(C−H)), 2055 (s, υ(CO)), 1969(s, υ(CO)), 1901 (s, υ(CO)), 1436 (s) and 1251 (s, υ(P═O)). UV/vis (CH_2Cl_2): λ_{max}: 254 nm. MS (EI, 70 eV): *m*/*z* (%) 376 (12) $[M-5CO]^+$, 325 (21) $[M-Cr(CO)_5]^+$, 91 (100) $[C_5H_3N_2]$. EA: calcd. for $C_{24}H_{21}CrN_2O_6P$: C 55.82, H 4.10, N 5.42 found: C 54.52, H 4.55, N 5.76.

[Pentacarbonyl(1-isopropyl-3-methyl-4-diphenylphosphoryl-imidazol-2-ylidene)molybdenum(0)] (11b). Yield: 0.33 g (0.6 mmol, 60%), yellow solid, mp 165 °C(dec.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.27 (d, $^3J_{H,H}$ = 6.7 Hz, 6H, $C_3H_7-CH_3$), 3.79 (s, 3H, N^3-CH_3), 5.26 (hept, $^3J_{H,H}$ = 6.6 Hz, 1H, C_3H_7-CH), 6.60 (d, $^3J_{P,H}$ = 1.9 Hz, 1H, C^5-H), 7.43−7.69 (m, 10H, C_6H_5-H). $^{13}C\{^1H\}$ NMR (75.0 MHz, $CDCl_3$): δ = 22.6 (s, C_3H_7-CH_3), 38.4 (d, $^3J_{P,C}$ = 1.2 Hz, N^3-CH_3), 52.7 (s, C_3H_7-CH), 126.8 (d, $^2J_{P,C}$ = 22.1 Hz, C^5), 127.8 (d, $^1J_{P,C}$ = 120.3 Hz, C^4), 128.1 (d, $J_{P,C}$ = 12.7 Hz, C_6H_5), 129.4 (d, $^1J_{P,C}$ = 112.3 Hz, *ipso*-C_6H_5), 130.5 (d, $J_{P,C}$ = 10.4 Hz, C_6H_5), 132.0 (d, $J_{P,C}$ = 2.9 Hz, C_6H_5), 194.7 (d, $J_{P,C}$ = 0.7 Hz, C^2), 204.9 (*cis*-CO), 209.1 ($trans\text{-}CO_{trans}$). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 15.8 (quint br, $^3J_{P,H}$ = 12.9 Hz). IR (KBr, cm^{-1}): $\tilde{\upsilon}$ = 3123 and 3076 (w, υ(C−H)), 2063 (s, υ(CO)), 1974(s, υ(CO)), 1905 (s, υ(CO)), 1438 (s) and 1252 (s, υ(P═O)).UV/vis (CH_2Cl_2): λ_{max}: 257 nm. MS (EI, 70 eV): *m*/*z* (%) 281 (12) $[C_{16}H_{14}N_2OP]^+$, 201 (38) $[C_{12}H_{10}OP]^+$, 82 (100) $[C_4H_6N_2]^+$. EA: calcd. for $C_{24}H_{21}MoN_2O_6P$: C 51.44, H 3.78, N 5.00 found: C 50.38, H 3.98, N 5.55.

[Pentacarbonyl(1-isopropyl-3-methyl-4-diphenylphosphoryl-imidazol-2-ylidene)tungsten(0)] (12b). Yield: 0.49 g (0.76 mmol, 76%), yellow solid, mp 178 °C(dec.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.33 (d, $^3J_{H,H}$ = 6.8 Hz, 6H, $C_3H_7-CH_3$), 3.85 (s, 3H, N^3-CH_3), 5.18 (hept, $^3J_{H,H}$ = 6.5 Hz, 1H, C_3H_7-CH), 6.65 (d, $^3J_{P,H}$ = 2.0 Hz, 1H, C^5-H), 7.51−7.75 (m, 10H, C_6H_5-H). $^{13}C\{^1H\}$ NMR (75.0 MHz, $CDCl_3$): δ = 22.6 (s, C_3H_7-CH_3), 39.3 (d, $^3J_{P,C}$ = 1.2 Hz, N^3-CH_3), 53.7 (s, C_3H_7-CH), 126.7 (d, $^2J_{P,C}$ = 22.0 Hz, C^5), 127.7 (d, $^1J_{P,C}$ = 120.2 Hz, C^4), 128.2 (d, $J_{P,C}$ = 12.7 Hz, C_6H_5), 129.2 (d, $^1J_{P,C}$ = 112.1 Hz, *ipso*-C_6H_5), 130.5 (d, $J_{P,C}$ = 10.8 Hz, C_6H_5), 132.1 (d, $J_{P,C}$ = 2.9 Hz, C_6H_5), 186.2 (d, $J_{P,C}$ = 1.0 Hz, C^2), 196.4 (s_{sat}, $^1J_{C,W}$ = 126.3 Hz, *cis*-CO), 199.7 (s_{sat}, $^1J_{C,W}$ = 132.6 Hz, *trans*-CO). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 16.0 (quint br, $^3J_{P,H}$ = 12.6 Hz). IR (KBr, cm^{-1}): $\tilde{\upsilon}$ = 3131 and 3082 (w, υ(C−H)), 2061 (s, υ(CO)), 1965(s, υ(CO)), 1897 (s, υ(CO)), 1438 (s) and 1254 (s, υ(P═O)),UV/vis (CH_2Cl_2): λ_{max}: 250 nm. MS (EI, 70 eV): *m*/*z* (%) 648 (36) $[M]^{\cdot+}$, 620 (36) $[M-CO]^+$, 589 (34) $[C_{20}H_{11}N_2O_6PW]^+$, 592 (100) $[M-2CO]^+$, 564 (50) $[M-3CO]^+$, 534 (36) $[M-4(CO)]^+$, 508 (58) $[M-5CO]^+$, 281 (48) $[C_{16}H_{14}N_2OP]^+$, 266 (12) $[C_{15}H_{11}N_2OP]^+$. EA: calcd. for $C_{24}H_{21}N_2O_6PW$: C 44.47, H 3.27, N 4.32 found: C 43.73, H 3.74, N 4.74.

[Pentacarbonyl(1-*n*-butyl-3-methyl-4,5-bis-(diphenylphosphoryl)imidazol-2-ylidene)chromium(0)] (13c). Yield: 0.51 g (0.7 mmol, 70%), yellow solid, mp 195 °C(dec.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.60 (t, $^3J_{H,H}$ = 7.3 Hz, 3H, $C_4H_9-CH_3$), 1.09−1.18 (m, 2H, $C_4H_9-CH_2$), 1.28−1.37 (m, 2H, $C_4H_9-CH_2$), 3.42 (s, 3H, N^3-CH_3), 4.85 (s br, 2H, $C_4H_9-CH_2$), 7.06−7.36 (m, 16H, C_6H_5-H), 7.43−7.50 (m, 4H, C_6H_5-H). $^{13}C\{^1H\}$ NMR (75.0 MHz, $CDCl_3$): δ= 13.4 ($C_4H_9-CH_3$), 19.5 ($C_4H_9-CH_2$), 34.7 ($C_4H_9-CH_2$), 41.2 (N^3-CH_3), 52.1 ($C_4H_9-CH_2$), 127.8 (d, $J_{P,C}$ =13.7 Hz, C_6H_5), 128.9 (d, $J_{P,C}$ =13.5 Hz, C_6H_5), 129.2 (d, $^1J_{P,C}$ =114.7 Hz, *ipso*-C_6H_5), 131.0 (d, $^1J_{P,C}$ =114.4 Hz, *ipso*-C_6H_5), 131.3 (d, $J_{P,C}$ =10.6 Hz, C_6H_5), 132.1 (d, $J_{P,C}$ =2.9 Hz, C_6H_5), 132.3 (d, $J_{P,C}$ =10.7 Hz, C_6H_5), 132.7 (d, $J_{P,C}$ =3.0 Hz, C_6H_5), 136.4 (d, $^1J_{P,C}$ =110.0 Hz, $^2J_{P,C}$ =17.6 Hz, C^4/C^5), 137.7 (d, $^1J_{P,C}$ =104.1 Hz, $^2J_{P,C}$ =18.7 Hz, C^5/C^4), 204.6 (s br, C^2), 216.9 (*cis*-CO), 221.1 (*trans*-CO_t).^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 25.0 (quint, $^3J_{P,H}$ = 12.5 Hz), 21.3 (quint, $^3J_{P,H}$ = 12.5 Hz). IR (KBr, cm^{-1}): $\tilde{\upsilon}$ = 2988 (w, υ(C−H)), 2065 (s, υ(CO)), 1970(s, υ(CO)), 1905 (s, υ(CO)), 1439 (s) and 1254 (s, υ(P═O)). UV/vis (CH_2Cl_2): λ_{max}: 244 nm. MS (EI, 70 eV): *m*/*z* 201 (100) $[Ph_2PO]^+$, 77 (12) $[Ph]^+$.

[Pentacarbonyl(1-*n*-butyl-3-methyl-4,5-bis-(diphenylphosphoryl)imidazol-2-ylidene)-molybdenum(0)] (14c). Yield: 0.55 g (0.72 mmol, 72%), yellow solid, mp 190 °C(dec.). ^{1}H NMR (300 MHz, $CDCl_3$): δ =0.62 (t, $^3J_{H,H}$ =7.2 Hz, 3H, $C_4H_9-CH_3$), 1.07−1.23 (m, 2H, $C_4H_9-CH_2$), 1.28−1.41 (m, 2H, $C_4H_9-CH_2$), 3.40 (s, 3H, N^3-CH_3), 4.85 (s br, 2H, $C_4H_9-CH_2$), 7.13−7.37 (m, 16H, C_6H_5-H), 7.61−7.77 (m, 4H, C_6H_5-H). $^{13}C\{^1H\}$ NMR (75.0 MHz, $CDCl_3$): δ = 12.4 ($C_4H_9-CH_3$), 18.6 ($C_4H_9-CH_2$), 33.4 ($C_4H_9-CH_2$), 40.9 (N^3-CH_3), 51.9 ($C_4H_9-CH_2$), 126.8 (d, $J_{P,C}$ = 14.0 Hz, C_6H_5), 127.9 (d, $J_{P,C}$ =13.0 Hz, C_6H_5), 128.2 (d, $^1J_{P,C}$ = 114.5 Hz, *ipso*-C_6H_5), 128.9 (d, $^1J_{P,C}$ = 114.2 Hz, *ipso*-C_6H_5), 130.4 (d, $J_{P,C}$ =10.6 Hz, C_6H_5), 131.2 (d, $J_{P,C}$ = 2.9 Hz, C_6H_5), 131.4 (d, $J_{P,C}$ = 10.8 Hz, C_6H_5), 131.8 (d, $J_{P,C}$ = 2.9 Hz, C_6H_5), 132.1 (d, $^1J_{P,C}$ = 110.5 Hz, $^2J_{P,C}$ = 17.9 Hz, C^4/C^5), 132.7 (d, $^1J_{P,C}$ =105.1 Hz, $^2J_{P,C}$ =18.3 Hz, C^5/C^4), 199.9 (s br, C^2), 204.8 (*cis*-CO), 210.3 (*trans*-CO).^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 25.2 (quint, $^3J_{P,H}$ = 12.3 Hz), 21.4 (quint, $^3J_{P,H}$ = 12.3 Hz). IR (KBr, cm^{-1}): $\tilde{\upsilon}$ = 2960 (w, υ(C−H)), 2064 (s, υ(CO)), 1979(s, υ(CO)), 1929 (s, υ(CO)), 1437 (s) and 1208 (s, υ(P═O)).UV/vis (CH_2Cl_2): λ_{max}: 252 nm. Pos.-ESI-MS: $C_{37}H_{32}MoN_2NaO_7P_2^+$ calcd (found) 799.1 (7999.1).

[Pentacarbonyl(1-*n*-butyl-3-methyl-4,5-bis-(diphenylphosphoryl)imidazol-2-ylidene)tungsten(0)] (15c). Yield: 0.56 g (0.65 mmol, 65%), yellow solid, mp 198 °C (dec.). ^{1}H NMR (300 MHz, $CDCl_3$): δ =0.68 (t, $^3J_{H,H}$ =7.4 Hz, 3H, $C_4H_9-CH_3$), 1.11 (m, 2H, $C_4H_9-CH_2$), 1.58 (m, 2H, $C_4H_9-CH_2$), 3.58 (s, 3H, N^3-CH_3), 4.41 (s br, 2H, $C_4H_9-CH_2$), 7.19−7.50 (m, 20H, C_6H_5-H). $^{13}C\{^1H\}$ NMR (75.0 MHz, $CDCl_3$): δ= 12.2 ($C_4H_9-CH_3$), 18.5 ($C_4H_9-CH_2$), 31.7 ($C_4H_9-CH_2$), 37.6 (N^3-CH_3), 50.5 ($C_4H_9-CH_2$), 127.5 (d, $J_{P,C}$ =13.6 Hz, C_6H_5), 128.1 (d, $J_{P,C}$ =13.6 Hz, C_6H_5), 128.6 (d, $^1J_{P,C}$ =114.9 Hz, *ipso*-C_6H_5), 129.0 (d, $^1J_{P,C}$ =114.7 Hz, *ipso*-C_6H_5), 130.8 (d, $J_{P,C}$ =11.3 Hz, C_6H_5), 131.3 (d, $J_{P,C}$ = 11.3 Hz, C_6H_5), 132.4 (d, $J_{P,C}$ =3.0 Hz, C_6H_5), 132.7 (d, $J_{P,C}$ = 3.0 Hz, C_6H_5), 133.1 (d, $^1J_{P,C}$ =110.6 Hz, $^2J_{P,C}$ =17.9 Hz, C^4/C^5), 133.7 (d, $^1J_{P,C}$ =105.6 Hz, $^2J_{P,C}$ =18.9 Hz, C^5/C^4), 190.1 (s br, C^2), 196.6 (s_{sat}, $^1J_{C,W}$ = 126.8 Hz, *cis*-CO), 198.4 (s_{sat}, $^1J_{C,W}$ = 131.3 Hz, *trans*-CO).^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 22.1 (quint, $^3J_{P,H}$ = 13.2 Hz), 24.9 (quint, $^3J_{P,H}$ = 13.2 Hz). IR (KBr, cm^{-1}): $\tilde{\upsilon}$ = 2962(w, υ(C−H)), 2063 (s, υ(CO)), 1973(s, υ(CO)), 1909 (s, υ(CO)), 1437 (s)and 1203 (s, υ(P═O)).UV/vis (CH_2Cl_2): λ_{max}: 231 nm. Pos.-ESI-MS: $C_{37}H_{32}N_2NaO_7P_2W^+$ calcd (found) 885.10 (885.11).

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[Pentacarbonyl(1,3-dimethyl-4,5-bis(diphenylphosphoryl)-imidazol-2-ylidene)tungsten(0)] (16a). Orange solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.67 (s, 6H, N−CH_3), 7.25−7.58 (m, 20H, C_6H_5−H). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 22.7 (quint, $^{3}J_{P,H}$ = 13.1 Hz). **16a** precipitated in little amounts only after keeping the crude mixture in diethyl ether over 4 days at low temperature (−20 °C), of which ^{1}H and ^{31}P NMR spectra were obtained and single-crystal X-ray diffraction studies was performed.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data for compounds **4b**, **8a**, **15c**, and **16a**, along with a cif file. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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