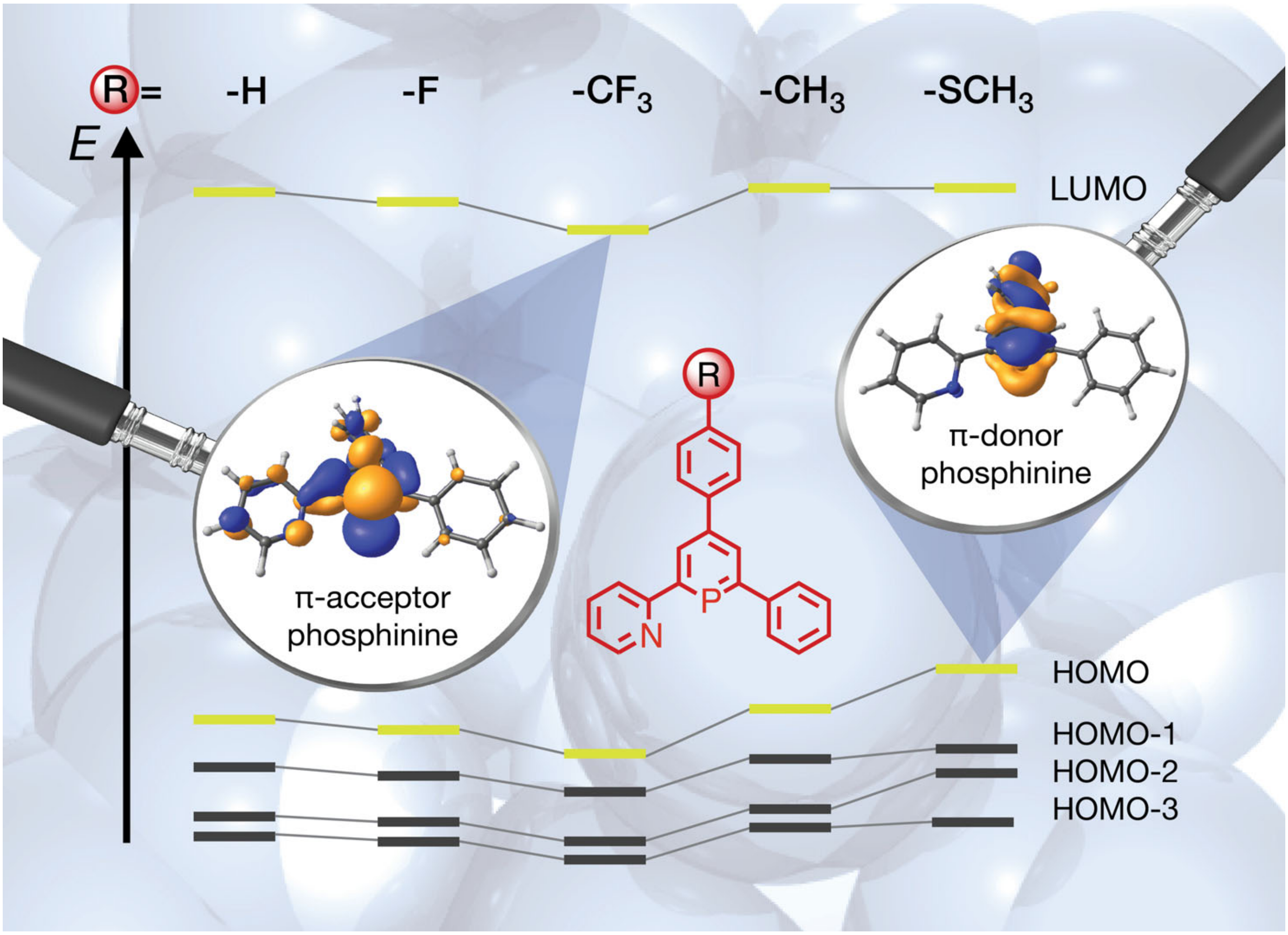


Showcasing research from the Institute of Chemistry and Biochemistry, Free University of Berlin, Berlin, Germany.

Tuning the electronic effects of aromatic phosphorus heterocycles: an unprecedented phosphinine with significant P(π)-donor properties

The novel methylthiol-substituted 2,4,6-triarylphosphinine derivative shows considerable π-donor properties as a result of the rather strong +M effect of the CH_3S-group. This unprecedented situation opens up the possibility to tune the electronic properties of such aromatic phosphorus heterocycles effectively with respect to potential applications in homogeneous catalysis and molecular material sciences.

As featured in:

See Christian Müller *et al.*,
Chem. Commun., 2014, **50**, 8842.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

ChemComm

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Chem. Commun.*, 2014, 50, 8842

Received 8th May 2014,
Accepted 6th June 2014

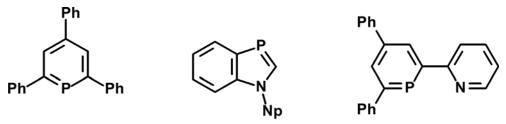
DOI: 10.1039/c4cc03469d

www.rsc.org/chemcomm

Tuning the electronic effects of aromatic phosphorus heterocycles: an unprecedented phosphinine with significant P(π)-donor properties†

Antonia Loibl,[a] Iris de Krom,[b] Evgeny A. Pidko,[c] Manuela Weber,[a] Jelena Wiecko[a] and Christian Müller*[ab]

A hitherto unprecedented electronic situation has been observed for a substituted, pyridyl-functionalized phosphinine. In contrast to previous studies, this compound shows considerable π-donor properties as the result of the rather strong +M effect of the CH_3S-substituent, changing the electronic properties of this low-coordinate and aromatic phosphorus heterocycle substantially.



A B 3a

Fig. 1 Low-coordinated $\lambda^3\sigma^2$-phosphorus compounds.

Since the first successful preparation of 2,4,6-triphenylphosphinine (A, Fig. 1) by Märkl in 1966, this low-coordinate phosphorus compound has been regarded as an aromatic heterocycle with significantly different electronic properties compared to its nitrogen counterpart (pyridine), as well as classical trivalent phosphorus(III) species.[1]

Both the reluctance of phosphorus to undergo 3s–3p hybridization and the differences in electronegativities of N (3.1), P (2.1) and C (2.5) lead to a substantial decrease in lone-pair basicity in C_5H_5P (63.8% lone-pair s-character) compared to C_5H_5N (29.1% lone-pair s-character). This special situation causes an inversion of the π-and n-orbital sequences between phosphinine and pyridine (Fig. 2).[2]

When coordinated to a metal center through the P-atom, phosphinines have been described to act as weak σ-donor (energetically low-lying HOMO−2), but rather strong π-acceptor (energetically low-lying LUMO) ligands, which can stabilize efficiently metal centers in low oxidation states.[3] In contrast, the π-excess aromatic $\lambda^3\sigma^2$-benzazaphospholes (B, Fig. 1), investigated by Heinicke *et al.*, show considerable P(π)-donor properties due to a $N^-{-}C{=}P \leftrightarrow N^+{=}C{-}P^-$ conjugation.[4] As a matter of fact, IR-stretching frequencies of transition metal carbonyl complexes of phosphinines indicate that these aromatic heterocycles act indeed as electron withdrawing ligands with properties similar to phosphites. Interestingly, their π-accepting behaviour has led to the development of very active Rh-catalysts for the hydroformylation of (internal) alkenes.[5] It has further been suggested that the HOMO and HOMO−1 π-orbitals can participate in η^6-coordination towards a transition metal center *via* the aromatic ring, which accounts for the range of coordination modes observed in various transition metal complexes based on phosphinines.[6]

With respect to potential applications, it has long been discussed whether or not only the steric but also the electronic properties of phosphinines can be modified successively. From the MO diagram shown in Fig. 2 it is, for example, not obvious why potentially π-donor properties of σ-coordinated phosphinines have neither been considered, nor discussed in the literature. Especially as the HOMO is rather high in energy, this situation should have a

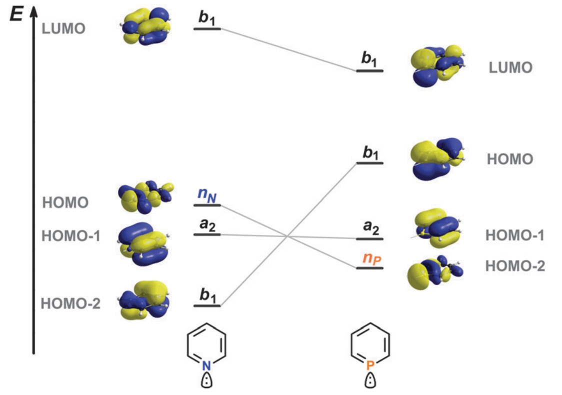


Fig. 2 Frontier orbitals of pyridine (left) and phosphinine (right).

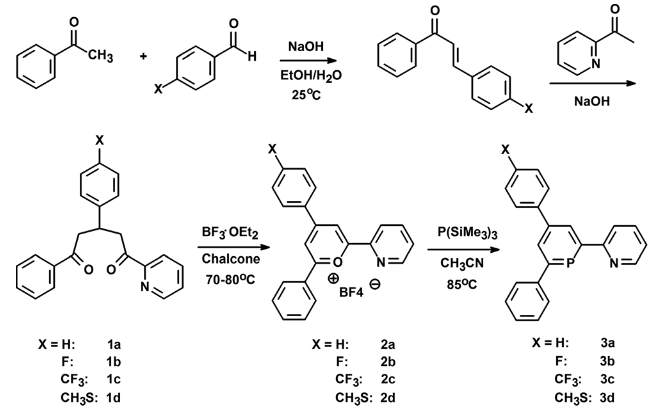
---

[a] *Institut für Chemie und Biochemie, Freie Universität Berlin, Fabeckstr. 34/36, 14195 Berlin, Germany. E-mail: c.mueller@fu-berlin.de; Fax: +49 30 838 454004; Tel: +49 30 838 54004*

[b] *Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Den Dolech 2, 5600 MB Eindhoven, The Netherlands*

[c] *Institute of Complex Molecular Systems, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*

† Electronic supplementary information (ESI) available: X-ray data and electrochemical data. CCDC 988905. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc03469d

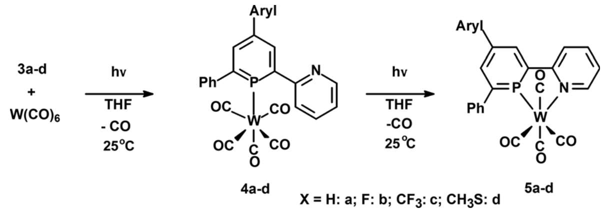


Scheme 1 Synthetic route towards substituted, pyridyl-functionalized phosphinines.

significant effect on the nature of the metal–phosphorus bond. On the other hand, a systematic investigation into the influence of substituents on the electronic properties of phosphinines has so far remained elusive, mainly due to synthetic reasons. During the course of our investigations into chelating phosphinines, we recently reported on the preparation and coordination chemistry of 2-(2′-pyridyl)-4,6-diphenylphosphinine, which was obtained *via* the classical pyrylium-salt route (**3a**, Scheme 1).[7] This P,N-hybrid ligand enforced σ-coordination to a metal center and is therefore an ideal bidentate ligand to probe influences of substituents on the electronic properties of the aromatic phosphorus heterocycle, because π-coordination can be excluded. We anticipated that the modular synthetic route towards **3a** would offer the possibility of introducing defined substituents into the phenyl group in the 4-position of the heterocyclic framework. This would allow for the first time a systematic modulation of the electronic properties of **3a** not only *via* +/−I-effects of the substituents, but also through the participation of the P=C double bond in conjugative interactions *via* +/−M-effects. Starting from *p*-substituted benzaldehydes, the corresponding diketones **1a–d** were synthesized by condensation reaction of the substituted chalcones with acetylpyridine. Subsequently, the pyrylium salts **2a–d**, bearing either a H, F, CF_3, or CH_3S-group could be obtained as yellow-red solids in good yields. We were able to convert all pyrylium-salts into the corresponding phosphinines **3a–d** by reaction with $P(SiMe_3)_3$ in CH_3CN (Scheme 1), although the isolated yields of the products were rather low.[8]

Compounds **3a–d** show the characteristic downfield-shift of the phosphorus-signal in the $^{31}P\{^1H\}$ NMR spectrum at *δ*(ppm) = 186.7 (**3a**), 186.6 (**3b**), 192.2 (**3c**) and 185.8 (**3d**). In order to probe the electronic properties of **3a–d** we decided to prepare the corresponding [W(κ-P,κ-N)$(CO)_4$] complexes and to analyze them by means of IR-spectroscopy. According to ^{31}P NMR spectroscopy, coordination compounds **5a–d** were obtained quantitatively by reaction of equimolar amounts of the ligand and $W(CO)_6$ in THF and under irradiation with UV-light (Scheme 2).

The reactions could be monitored by means of $^{31}P\{^1H\}$ NMR spectroscopy and the course of the reaction is depicted for the fluorine-substituted P,N-ligand **3b** in Fig. 3.



Scheme 2 Synthesis of phosphinine-based tungsten(0) complexes.

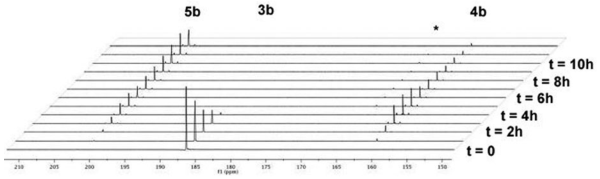


Fig. 3 Time-dependent $^{31}P\{^1H\}$ spectra for the conversion of phosphinine **3b** with $W(CO)_6$ towards **5b**. * Unidentified species.

Interestingly, an intermediate with W-satellites ($^1J_{P–W}$ = 275 Hz) is observed at *δ*(ppm) = 160.8 upon consumption of the ligand, while the final complex **5b** has been formed almost quantitatively after 10 h (*δ*(ppm) = 201.0, $^1J_{P–W}$ = 278 Hz). We assume that the observed intermediate is the mono-coordinated pentacarbonyl-species [W(κ-P,N)$(CO)_5$] **4b**, depicted in Scheme 2. A similar transient species has been observed by Mathey *et al.* upon reaction of NIPHOS with *in situ* generated [$W(CO)_5THF$].[9,10]

All complexes could be isolated as red solids after recrystallization and were analyzed by means of NMR spectroscopic techniques. Red crystals of the fluorine-substituted compound **5b** suitable for X-ray diffraction were obtained from a hot THF solution. The compound crystallizes in the orthorhombic space group $Pna2_1$ and the molecular structure is depicted in Fig. 4 along with selected bond lengths and angles. The molecular structure of **5b** in the crystal shows a distorted octahedral coordination geometry around the W-center with the P,N-hybrid ligand acting as a bidentate chelate. As observed before in related transition metal complexes of the unsubstituted P,N-ligand **3a**, the metal center is not located in the ideal axis of the phosphorus lone-pair and clearly shifted towards the nitrogen atom.

Coordination compounds **5a–d** were further investigated by means of IR-spectroscopy (Table 1). In agreement with related bypridine–$W(CO)_4$ compounds, all complexes show the characteristic wavenumbers $\tilde{\nu}_{(CO)}$ centered at around 1900 cm^{-1}. For the fluorine-substituted derivative **5b** we noticed only a

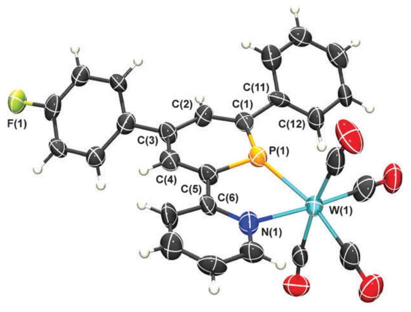


Fig. 4 Molecular structure of **5b** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): W(1)–P(1): 2.464(4); W(1)–N(1): 2.31(2); P(1)–C(1): 1.77(2); P(1)–C(5): 1.72(2); C(5)–C(6): 1.49(2); C(1)–P(1)–C(5): 104.1(8).

Table 1 IR-wavenumbers $\tilde{\nu}_{(CO)}$ of **5a–d** [in cm^{-1}]

	5a (–H)	**5b** (–F)	**5c** ($-CF_3$)	**5d** ($-SCH_3$)
$\tilde{\nu}_1$	2008	2012	2014	2014
$\tilde{\nu}_2$	1893	1893	1920	1971
$\tilde{\nu}_3$	1870	1877	n.d.	1889
$\tilde{\nu}_4$	1836	1840	1857	1858

marginal shift to higher wavenumbers compared to the reference compound **5a** (R = H). We attribute this minor increase in the π-acceptor capacity of the phosphinine **3b** to a +M effect of the fluorine atom, which counterbalances the –I effect of this electron-withdrawing substituent. Indeed, the IR-data of compound **5c**, which bears a $-CF_3$ as a pure –I substituent in the *para*-position, proved the higher π-accepting properties of ligand **3c**. In the presence of an electron-donating group in the same position of the heterocycle, one would expect a shift to lower wavenumbers due to an increased electron density in the antibonding π*(C–O) orbitals. Much to our surprise, however, we clearly observed a significant opposite effect for coordination compound **5d**, which contains a CH_3S-substituent in the *para*-position. As a matter of fact, we detected a considerable shift of the IR bands to higher wavenumbers, rather than to lower ones. In order to explain this unusual observation we carried out DFT-calculations at the B3LYP/6-311+G(d,p) level on the pyridyl-functionalized phosphinines **3a–d** and compared the relative energies of the frontier orbitals. The results are depicted in Fig. 5. For comparison, we included the H_3C-substituted coordination compound in the calculations, although the corresponding P,N-ligand could not be synthesized.[8]

Fig. 5 (right side) shows the shape of the frontier orbitals of the CH_3S-substituted phosphinine **3d**. Qualitatively, both the sequence and the shape of the π- and n-orbitals resemble the ones depicted in Fig. 2 for the parent compound C_5H_5P with the exception that the HOMO−1 in C_5H_5P is now represented by the HOMO−1 and HOMO−2 in **3d**. This is also the case for phosphinines **3a–c**. Upon introducing a fluorine substituent (**3b**), the frontier orbitals are slightly stabilized. This is in line with our chemical intuition that the electron withdrawing fluorine substituent should lower the energy of the LUMO which would consequently lead to stronger π-accepting properties as observed also in the IR stretching frequencies in **5b**. This effect, however, seems to be only marginal and might be attributed to the +M effect of the fluorine substituent.

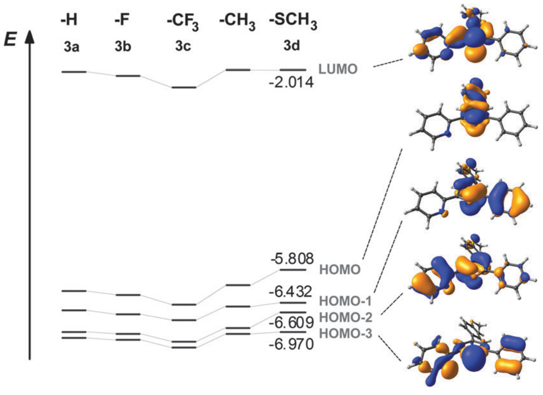


Fig. 5 Frontier orbitals of **3a–d** and the CH_3-derivative.

Remarkably, upon introducing a CH_3- or CH_3S-substituent (**3d**), the frontier orbitals are destabilized compared to the reference compound **3a**, while especially the HOMO is now much higher in energy than the HOMO in **3a**. We believe that the rather strong +M effect of especially the CH_3S-group increases the π-donor properties of **3d** by conjugative interactions through the HOMO. This situation leads consequently to an energetically high-lying HOMO and at the same time to stronger π-donor properties. However, this does not clarify why the IR-stretching frequencies in **5d** are shifted to higher wavenumbers compared to those in **5a**. We anticipate that the particular electronic properties of phosphinines might deliver a plausible explanation: in contrast to common π-donor ligands, such as halides, S^{2-} or SCN^- (see the spectrochemical series), the LUMO (π-accepting properties) and the HOMO (π-donating properties) in **3d** have particularly large coefficients at the phosphorus donor-atom, which are similar in shape and which point to the same direction (Fig. 5). These molecular orbitals would therefore interact with the same filled metal-centered d-orbital in an octahedral complex, leading to repulsion and net weakening of the P–M bond and, consequently, to a shift of the IR stretching modes to higher wavenumbers, *i.e.* close to uncomplexed $W(CO)_6$ ($\tilde{\nu}$ = 1998 cm^{-1}).

We have demonstrated that the electronic properties of 2,4,6-triarylphosphinine derivatives can be modulated systematically and rather efficiently by introducing substituents into specific positions of the heterocyclic framework. Furthermore, we found evidence that the HOMO and HOMO−1 of π-symmetry play a significant role in the properties of metal complexes containing σ-coordinated phosphinine ligands, which has so far been neglected for this class of compounds. This particular electronic situation is caused by the special shape and orientation of the LUMO and the HOMO of the phosphinine ligand and is unique in comparison with other π-donors.

The European Initial Training Network SusPhos (317404) is gratefully acknowledged for financial support.

Notes and references

1 (*a*) G. Märkl, *Angew. Chem.*, 1966, **78**, 907; (*b*) G. Märkl, in *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, ed. M. Regitz and O. J. Scherer, Thieme Verlag, Stuttgart, 1990, pp. 220–257.
2 (*a*) C. Batich, E. Heilbronner, V. Hornung, A. J. Ashe III, D. T. Clark, U. T. Gobley, D. Kilcast and I. Scanlan, *J. Am. Chem. Soc.*, 1973, **95**, 929; (*b*) N. Mézailles, F. Mathey and P. Le Floch, *Prog. Inorg. Chem.*, 2001, 455.
3 (*a*) C. Müller, L. E. E. Broeckx, I. de Krom and J. J. M. Weemers, *Eur. J. Inorg. Chem.*, 2013, 187; (*b*) P. Le Floch, *Coord. Chem. Rev.*, 2006, **250**, 627; (*c*) P. Le Floch and F. Mathey, *Coord. Chem. Rev.*, 1998, **179–180**, 771; (*d*) C. Müller and D. Vogt, *Dalton Trans.*, 2007, 5505.
4 (*a*) M. Ghalib, L. Könczöl, L. Nyulászi, P. G. Jones, G. J. Palm and J. W. Heinicke, *Dalton Trans.*, 2014, **43**, 51; (*b*) M. Ghalib, P. G. Jones, G. J. Palm and J. W. Heinicke, *RSC Adv.*, 2013, **3**, 17726.
5 (*a*) B. Breit, R. Winde, T. Mackewitz, R. Paciello and K. Harms, *Chem. – Eur. J.*, 2001, **7**, 3106; (*b*) L. Kollár and G. Keglevich, *Chem. Rev.*, 2010, **110**, 4257.
6 E. F. DiMauro and M. C. Kozlowski, *J. Chem. Soc., Perkin Trans. 1*, 2002, 439.
7 I. de Krom, E. A. Pidko, M. Lutz and C. Müller, *Chem. – Eur. J.*, 2013, **19**, 7523.
8 Unfortunately, the pyrylium salt of the $-CH_3$-substituted derivative could not be obtained in a pure form.
9 A. Brèque, C. C. Santini, F. Mathey, J. Fischer and A. Mitschler, *Inorg. Chem.*, 1984, **23**, 3463.
10 J. Deberitz and H. Nöth, *J. Organomet. Chem.*, 1973, **49**, 453.