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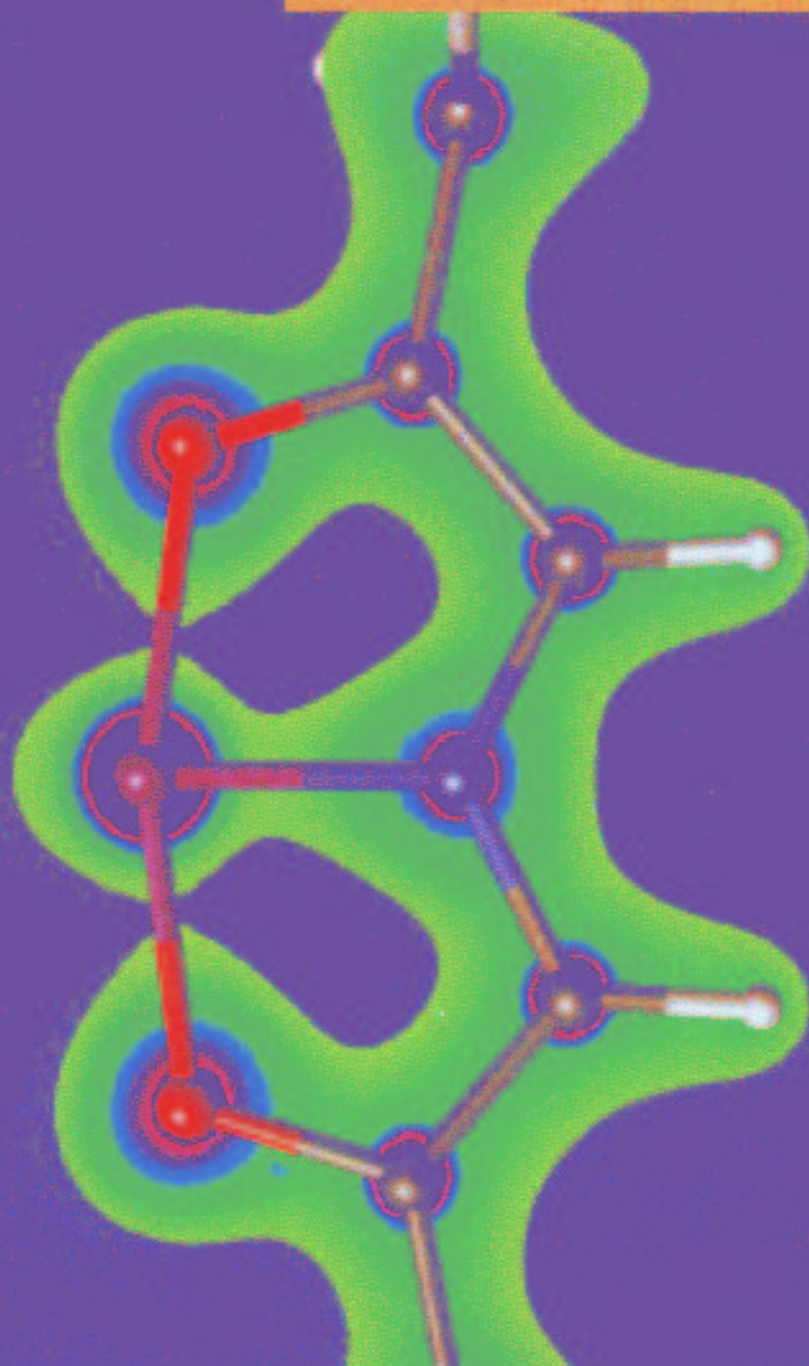
Focus:

Stable Silylenium
(Silicenium) Ions In
A Condensed Phase—
Dream or Reality?

Ten Years of Tricoordinate
Hypervalent Phosphorus
Chemistry

Diethanolamines,
Diphenolamines,
Diethylenetriamines—
The Game with
Phosphorus and Boron

49th Southwest Regional
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The B.A. Arbuzov
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Ten Years of Tricoordinate Hypervalent Phosphorus Chemistry[†]

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A s it was first reported in 1983, the reaction between the diketoamine ligand **1** and PCl_3 in the presence of triethylamine affords a unique 10-electron 3-coordinate phosphorus compound, ADPO (3,7-di-*tert*-butyl-5-aza-2,8-dioxa-1-phosphabicyclo[3.3.0]octa-2,4,6-triene) (Equation 1) [1, 2].

$$ \text{(1)} $$

1   **ADPO**
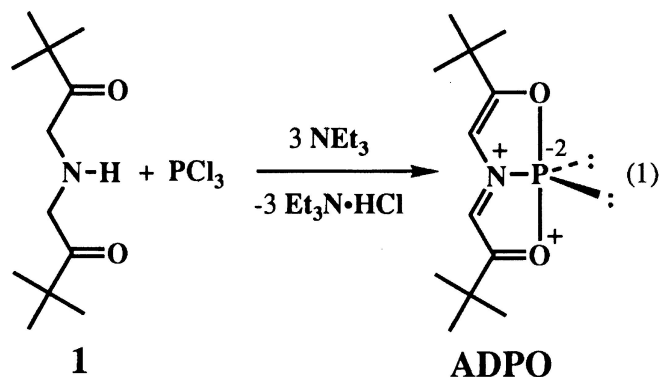
ADPO has been characterized by multinuclear NMR spectroscopy and its planar T-shaped geometry was confirmed by X-ray crystallography [2, 3]. The most intriguing aspect of ADPO is the stability of planar 10-P-3 hypervalent form over the more conventional folded 8-P-3 form which conforms to the octet rule (Equation 2) [4]. The special relationship between these two valence isomers is called electromorphism [5] and leads to some very unusual chemistry for the ADPO molecule. The stability of the planar 10-P-3 electromorph over its folded 8-P-3 isomer has been attributed to several key features of the ligand and a detailed discussion is recorded elsewhere [3]. It is known from theoretical studies that the energy difference between two electromorphs is very low and estimated to be about 13. 9 kcal/mol [6]. In fact, many electrophiles can disturb this delicate balance and give adducts of ADPO that appear to be derived from the higher energy 8-P-3 electromorph.

[†] DuPont Contribution No. 6811.

10-P-3 ADPO **8-P-3 ADPO**

(2)
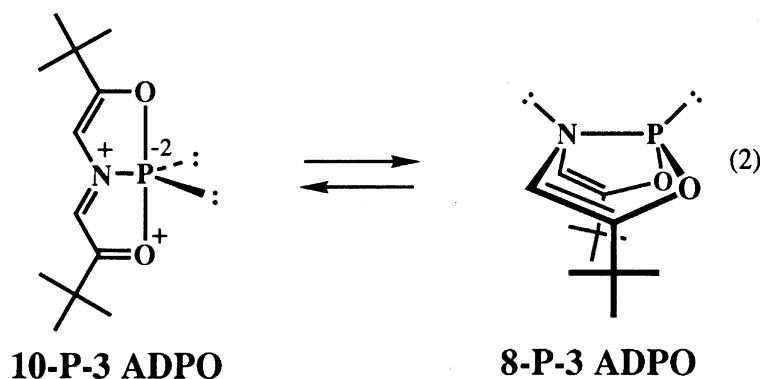
The phosphorus center in 10-P-3 ADPO has an oxidation state of I, while the phosphorus in the 8-P-3 electromorph of ADPO has an oxidation state of III [7]. The oxidation state of phosphorus in the 8-P-3 electromorph (III) is typical of many phosphines and phosphites. On the other hand, the oxidation state of phosphorus in 10-P-3 ADPO (I) seems unusual for a 3-coordinate phosphorus center. If the second lone pair of electrons at phosphorus in 10-P-3 ADPO is considered, it is evident that the oxidation state of phosphorus must be reduced by 2 from the value in 8-P-3 ADPO, where the phosphorus has only the single lone pair of electrons that is typically found in phosphines and phosphites. Another description of 10-P-3 ADPO which helps clarify this oxidation state problem is the hypothetical structure 2 that attempts to represent the hypervalent (3-center, 4-electron) bond in 10-P-3 ADPO as internal solvation of a phosphinidene (6-P-1, oxidation state I) center. On the cover is a cross-section of electron density in the molecular plane calcualted for the 3,7-dimethyl analog of ADPO [8]. The contours levels

are drawn between 0.75 eÅ^{-3} (yellow) and 10 eÅ^{-3} (red). The diminished electron density in the O-P-O hypervalent bond relative to other σ-bonds in the ring supports this alternative view of 10-P-3 ADPO as an internally solvated phosphinidene.

2
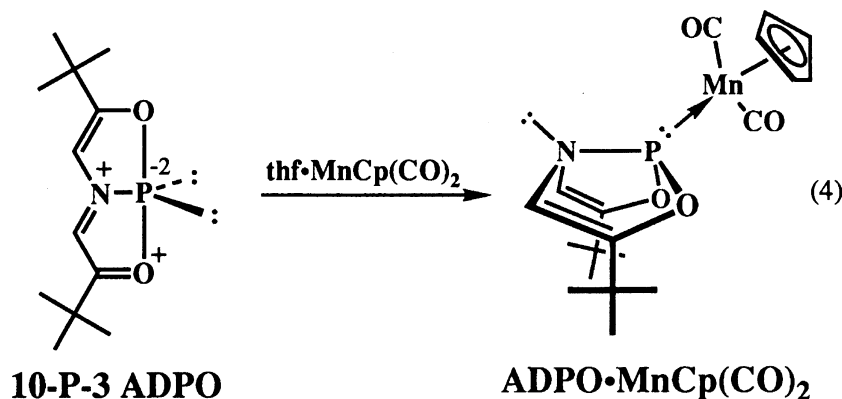**internally solvated**
phosphinidene
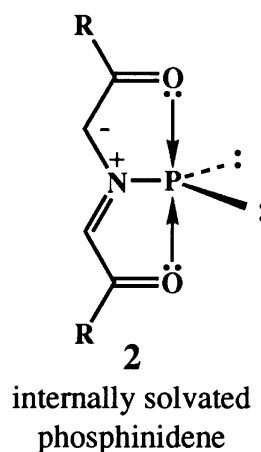
This oxidation state flexibility allows ADPO to show a rich variety of chemistry. It has been possible to demonstrate the chemical and/or stereochemical activity of both the lone pair of electrons at the phosphorus in 10-P-3 ADPO. The oxidation state flexibility within the ADPO molecule sometimes gives rise to an apparent 4-electron oxidation at phosphorus with 2-electron oxidants, as in the case of the oxidation with chlorine (Equation 3) [3]. This is a consequence of participation of the redox active ligand system which chelates the phosphorus of ADPO. The arsenic or antimony analogs of ADPO are not complicated by an intramolecular electron reorganization and have always shown chemistry arising from the 10-Pn-3 (Pn=pnictogen) electromorph.


P (I) **P (V)**

(3)
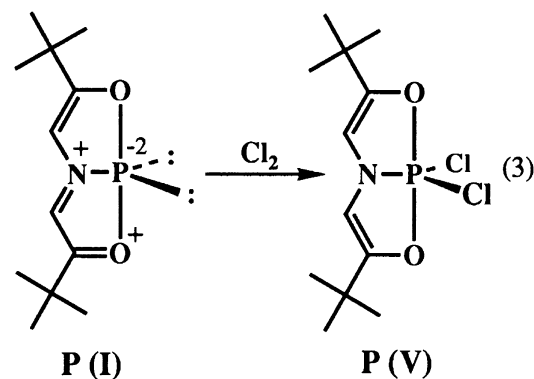
With transition metals, similar complications can also arise. For example, the reaction between $CpMn(CO)_2 \bullet (thf)$ and ADPO leads to the adduct $ADPO \bullet MnCp(CO)_2$ where the ADPO unit adopts a folded geometry (Equation 4) [9]. This process involves the transfer of electron density from the phosphorus center to the ligand backbone. The structure of $ADPO \bullet MnCp(CO)_2$ was confirmed by X-ray crystallography and shows a 117° fold angle for the ADPO unit [9]. In addition to the obvious geo-

metric changes, the ring folding can be detected conveniently using ^{1}H and ^{13}C NMR spectroscopy. Most significant changes are observed in the chemical shift values of $H_{4,6}$ and $C_{3,7}$, which show $\Delta\delta$'s of ~2 and ~15 ppm respectively, with the resonances for the folded adduct upfield of their counterparts in planar 10-P-3 ADPO [9]. Similar behavior is observed when ADPO is treated with several other transition metals, such as Cr(0) [10], W(0) [10], Fe(0) [11], Ru(I) [12] and Ni(0) [10].

$$\text{10-P-3 ADPO} \xrightarrow{\text{thf} \bullet \text{MnCp(CO)}_2} \text{ADPO} \bullet \text{MnCp(CO)}_2 \tag{4}$$

10-P-3 ADPO **ADPO•MnCp(CO)₂**

When two or more ADPO ligands coordinate to the same metal center it is possible to observe a dimerization of the folded ADPO units that is not possible for free 10-P-3 ADPO. This dimerization of folded ADPO units has been observed in some Pd(II) [10] and Fe(0) [11] complexes in which the ADPO groups can come sufficiently close for the intramolecular reaction to occur. Such a dimerization

actually occurs twice on the homoleptic ADPO complex of palladium(II), $Pd^{+2}[\{ADPO\}_2]_2(BF_4^-)_2$ (Equation 5). The dimeric ADPO unit, $\{ADPO\}_2$, can be released from $Pd^{+2}[\{ADPO\}_2]_2(BF_4^-)_2$ as a bidentate ligand by treatment with diphos or tetraphos [10]. This transient dimer slowly reverts to 10-P-3 ADPO but has been characterized spectroscopically [10, 13].

$$4\ ADPO + Pd^{+2}(CH_3CN)_4(BF_4^-)_2 \xrightarrow{-\ 4\ CH_3CN} \tag{5}$$

Pd⁺²[{ADPO}₂]₂(BF₄⁻)₂
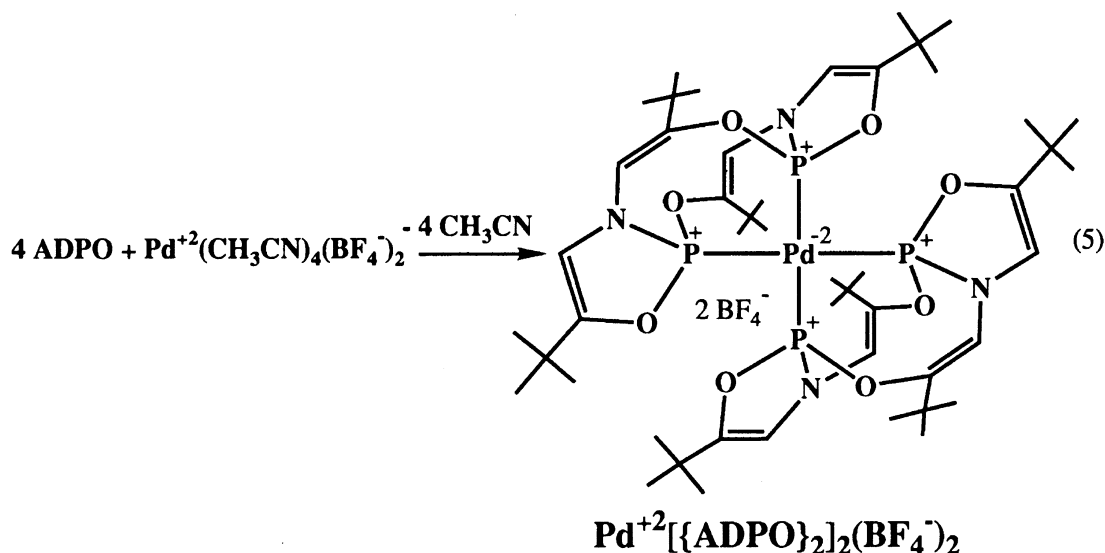
The reactivity of both phosphorus lone pairs of electrons in ADPO is only observed when the ADPO ring is not disturbed by more than the 14 kcal/mol that separate the 10-P-3 and 8-P-3 electromorphs [5]. Silver(I) is known to be a weak acceptor for phosphorus and provides the opportunity to observe activity for both of these phosphorus lone pairs. The treatment of ADPO with $Ag(CH_3CN)_4{}^+SbF_6{}^-$ in a 4:1 molar ratio leads to the homoleptic complex, $(ADPO)_4Ag^+SbF_6{}^-$ (Equation 6) [14]. Unlike the previously described metal complexes, these ADPO units retain their planar geometry and still possess a stereochemically active lone pair. The X-ray structure of $(ADPO)_4Ag^+SbF_6{}^-$ shows the four planar ADPO units and also a rather unusual square planar silver ion.

$$4 \ ADPO \ + \ (CH_3CN)_4Ag^+SbF_6{}^- \ \xrightarrow{-4 \ CH_3CN}$$

$$(ADPO)_4Ag^+ \ SbF_6{}^-$$

(6)
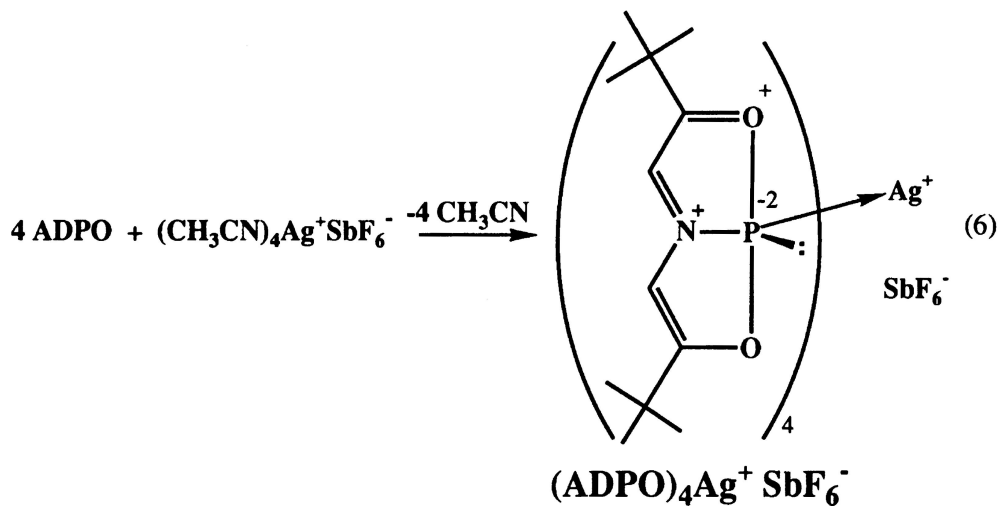
In addition to the geometry, which is obvious from the solid state X-ray structure of $(ADPO)_4Ag^+SbF_6{}^-$, solution NMR spectroscopy shows $\Delta\delta$ values for the ring protons (H4,6) and C3,7 that are much smaller (~0.4 and ~3.0 ppm, respectively) and in the opposite direction from other metal adducts. A variation of the reactant ratios (1:1) gives a polymeric complex, $([(ADPO)Ag(NCCH_3)_2]^+SbF_6{}^-)_n$, in which ADPO is coordinated to two silver ions using both of its phosphorus lone pairs (Equation 7). The crystal structure clearly shows the 10-P-5 arrangement. The four coordinate siver center in $([(ADPO)Ag(NCCH_3)_2]^+SbF_6{}^-)_n$ adopts the more common tetrahedral geometry.

$$ADPO \ + \ (CH_3CN)_4Ag^+SbF_6{}^- \ \xrightarrow{-2 \ CH_3CN}$$

$$(\ [(ADPO)Ag(NCCH_3)_2]^+SbF_6{}^-)_n$$

(7)
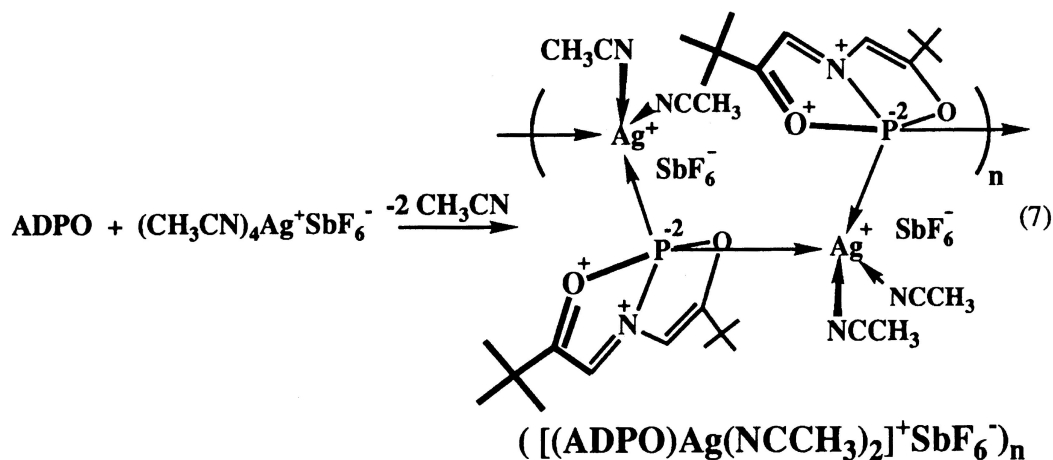
In conclusion, the above account briefly describes the chemistry of ADPO and some interesting aspects associated with electromorphism. This unique molecule behaves as a 2- or 4-electron donor, monodentate ligand, bidentate ligand (through dimerization) or a bridging ligand leading to a variety of unusual metal complexes. An overview of the coordination chemistry of ADPO along with some new metal chemistry was recently presented at a symposium [15] in honor of Alan H. Cowley and will be published in the conference proceedings [10]. A more complete review of all ADPO chemistry will appear shortly [13]. ❖

References and Notes

1. S.A. Culley and A.J. Arduengo, III, *Abstracts of Papers*, 186th National Meeting og the American Chemical Society, Washington, DC, ACS: Washington, DC, 1983; ORGN 109.
2. S.A. Culley and A.J. Arduengo, III, *J. Am. Chem. Soc.*, **106**, 1164 (1984).
3. A.J. Arduengo, III, et al., *J. Am. Chem. Soc.*, **109**, 627 (1987).
4. The *N-X-L* nomenclature system has been previously described (C. Perkins et al., *J. Am. Chem. Soc.*, **102**, 7753 (1980)). N valence electrons about a central atom X, with L ligands.
5. The term "electromorph" has been previously defined (ref. 2) and

refers to isomers with different electron distributions and different geometries (morphologies) but the same connectivity.
6. A.J. Arduengo, III and D.A. Dixon, "Electron Rich Bonding at Low Coordination Main Group Element Centers," in *Heteroatom Chemistry: ICHAC-2*; E. Block, ed., VCH: New York (1990).
7. The oxidation state of a central atom described by an N-X-L designator can be calculated as $|X|-(N-2L)$, where N and L have the usual meanings (number of bonding electrons [lone pairs + sigma bonds] and number of ligands, respectively) and $|X|$ is the number of valence electrons at the isolated atom X. Thus for 10-P-3 ADPO, the oxidation state of phosphorus is $5-(10-2(3))$ or 1. The oxidation state of phosphorus in 8-P-3 ADPO is $5-(8-2(3))$ or 3. The oxidation state of phosphorus in a 6-P-1 phosphinidene is $5-(6-2(1))$ or 1.
8. This drawing is the result of a Local Density Functional Theory (LDFT) calculation on 3,7-dimethyl-5-aza-2,8-dioxa-1-phospha-bicyclo[3.3.0]octa-2,4,6-triene. The calculation was done with the program DGauss (TZVP basis set), a density functional program available via the Cray Unichem Project. We appreciate the help and assistance of Dr. David A. Dixon and Scott C. Walker in making this picture.
9. A.J. Arduengo, III, et al., *J. Am. Chem. Soc.*, **113**, 1799 (1991).
10. A.J. Arduengo, III, et al., *Phos., Sulf., Sil. and the Related Elements* (in press) (1994).
11. A.J. Arduengo, III, et al., *Heteroat. Chem.*, **2**, 395 (1991).
12. A.J. Arduengo, III, et al., *Heteroat Chem.*, **1**, 407 (1990).
13. A.J. Arduengo, III and C.A. Stewart, *Chem Rev.*, **94** (in press) (1994).
14. A.J. Arduengo, III, et al., *J. Am. Chem. Soc.*, **113**, 7071 (1991).
15. A.J. Arduengo, III, et al., "Recent Coordination Chemistry of ADPO," Symposium on Recent Advances in the Chemistry of Main Group Elements, 49th Southwest Regional Meeting of the ACS, Austin, TX, Oct. 24-27, 1993, paper no. 79.