solution mixture (0.034 g, 59%); m.p. 136–137°C. ^{31}P{^{1}H} NMR (CDCl$_3$): $\delta = 309.7$, 79.9 (d, ^2J(P,P) = 192.5 Hz); ^{1}H NMR (CDCl$_3$): $\delta = 2.23$ (dd, ^3J(P,H) = 6.8, 23.0 Hz, 3H; C-CH$_3$); ^{13}C{^{1}H} NMR (CDCl$_3$): $\delta = 18.8$ (dd, ^2J(P,C) = 3.4, 3.7 Hz, C-CH$_3$), 109.7 (dd, ^1J(P,C) = 131.3, 64.5 Hz, PCP).

4: Tetrachloro-*o*-benzoquinone was added to a solution of **2** at −78°C and the resulting carbodiphosphorane **4** was crystallized from a toluene/pentane solution at −20°C as white crystals (0.031 g, 48%); m.p. 143–144°C. ^{31}P{^{1}H} NMR (C$_6$D$_6$): $\delta = 25.5$, 21.5 (d, ^2J(P,P) = 126.4 Hz); ^{13}C{^{1}H} NMR (C$_6$D$_6$): $\delta = 38.3$ (dd, ^1J(P,C) = 149.4, 187.2 Hz, P=C=P).

5: The nitrone Ph(H)C=N(O)*t*Bu was added to a solution of **2** at room temperature and the solution was heated at 55°C for 15 days. The cycloadduct **5** precipitated from an Et$_2$O/CH$_3$CN solution at −20°C as colorless crystals (0.051 g, 85%); m.p. 160–161°C. ^{31}P{^{1}H} NMR (CDCl$_3$): $\delta = 71.0$, 46.8 (d, ^2J(P,P) = 67.8 Hz); ^{13}C{^{1}H} NMR (CDCl$_3$): $\delta = 40.0$ (dd, ^1J(P,C) = 131.4, 17.5 Hz, P-C-P), 72.2 (dd, ^2J(P,C) = 14.7, 6.4 Hz, Ph-C-H).

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4,5-Bis(diphenylphosphinoyl)-1,2,3-triazole: A Powerful New Ligand That Uses Two Different Modes of Chelation

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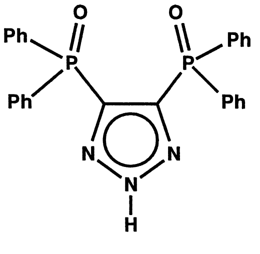
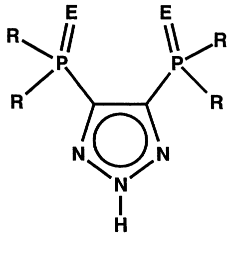
We report a novel and powerful ligand that is thermally, oxidatively, and hydrolytically very stable. It avidly forms complexes with cations through the adoption of two entirely different chelation modes, allowing the facile extraction of metal ions from aqueous systems. This novel ligand is the anion [L^T]$^-$ of 4,5-bis(diphenylphosphinoyl)-1,2,3-triazole L^{T}H, which combines the features of the coordinating ability of the P(O)Ph$_2$ groups with the nitrogen donor atoms of the triazole ring. Moreover, it is the prototype of a much broader family of ligands with the general structure L^X, in which E can



L^{T}H



L^X

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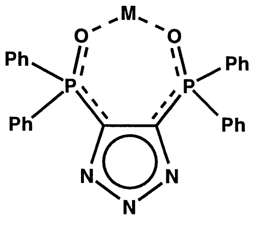
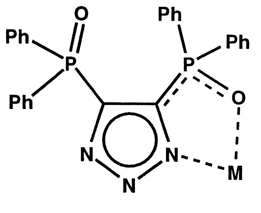
be S, Se, NR, or NAr, while R can be a variety of alkyl or aryl groups.

As can be seen from structures **A** and **B** there are two posssible modes of chelation for $[L^T]^-$: a symmetric one (C_{2v}), through the two O termini, forming a seven-membered chelate ring (**A**), and an asymmetric one, through one O and the nearest N, resulting in a five-membered chelate ring (**B**). In addition, nucleophilic reactivity is also possible through the central nitrogen. These chelation modes of $[L^T]^-$ are quite different from the six-membered chelate rings formed by the known $P(O)Ph_2$-containing β-diketonate analogues, such as those derived from the anions $HN[P(O)Ph_2]_2$,[1–3] $HC[P(O)Ph_2]_2$,[4] or 4-diphenylphosphinoyl-3-methyl-1-phenylpyrazolone.[5] Each of the chelating modes for L^T has been demonstrated, and pertinent key structures of type **A** and **B** have been established by X-ray crystallography.

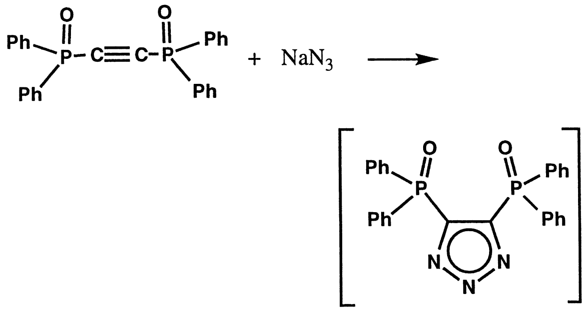


A



B

The sodium salt of L^TH, $Na[L^T]$, was obtained directly by the reaction of NaN_3 with bis(diphenylphosphinoyl)acetylene in methanol [Eq. (1)],[6] and this solution could be used directly for the preparation of metal chelates.



(1)

Acidification of the $Na[L^T]$ solution with HCl yielded the free acid L^TH, which melted sharply at 333–334 °C. It formed a halocarbon-soluble triethylamine salt, $[L^T][Et_3NH]$, used for reactions of the L^T ligand in organic solvents.

In an exploratory screening of the coordination behavior of $[L^T]^-$ with first-row transition metals, we found that Fe^{II}, Co^{II}, Ni^{II}, and Cu^{II} were readily extracted from aqueous solutions into chloroform or dichloromethane. The isolated solid chelates, the colors of which were suggestive of octahedral coordination, were also soluble in hot aromatic hydrocarbons, but crystals suitable for X-ray crystallographic determination could not be grown from these solvents. Considering that, regardless of the mode of chelation, there are still three additional donor atoms available from each L^T ligand, we assumed the presence of extended oligomeric or polymeric structures for all these species. The cobalt complex $[Co(L^T)_2]$ was recrystallized from pyridine, yielding the structurally characterized compound **1** (Figure 1) of composition $[Co(L^T)_2(py)_2]\cdot 2\,py$ (py = pyridine). In **1**, the cobalt ion was N,O-bonded in a square-planar configuration to two L^T ligands, and also to two apical pyridine N donors. The two L^T ligands were coordinated in *trans* fashion.

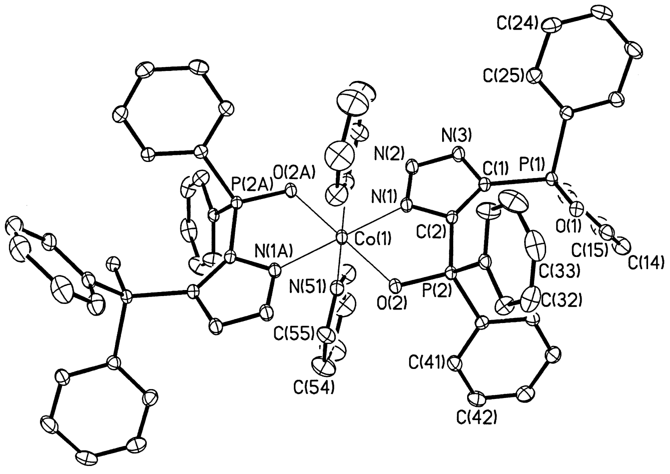


Figure 1. Molecular structure of $[Co(L^T)_2(py)_2]\cdot 2\,py$ (**1**) (30 % thermal ellipsoids). Selected bond lengths [Å] and angles [°]: Co(1)-N(1) 2.122(2), Co(1)-O(2) 2.121(1), Co(1)-N(51) 2.203(2); N(1)-Co(1)-O(2) 82.17(6), N(1)-Co(1)-O(2a) 97.83(6), N(51)-Co(1)-O(2) 88.85(7), N(51)-Co(1)-N(1) 92.24(7); *trans* angles at Co(1) 180.

The same κ^2 N,O-mode of chelation was found in other structurally characterized complexes, such as $[Rh(L^T)(cod)]$ (**2**; cod = 1,5-cyclooctadiene; Figure 2), produced by the reaction of $[L^T][Et_3NH]$ with $[\{Rh(cod)Cl\}_2]$, as well as in the heteroleptic five-coordinate complexes $[Co(L^T)(Tp^{\alpha Nt})]$ (**3**; Figure 3), and $[Ni(L^T)(Tp^{iPr,4Br})]$ (**4**; Figure 4), obtained by the reaction of $[L^T][Et_3NH]$ with $Co[Tp^{\alpha Nt}]Cl$ and $Ni[Tp^{iPr,4Br}]Cl$, respectively.[7]

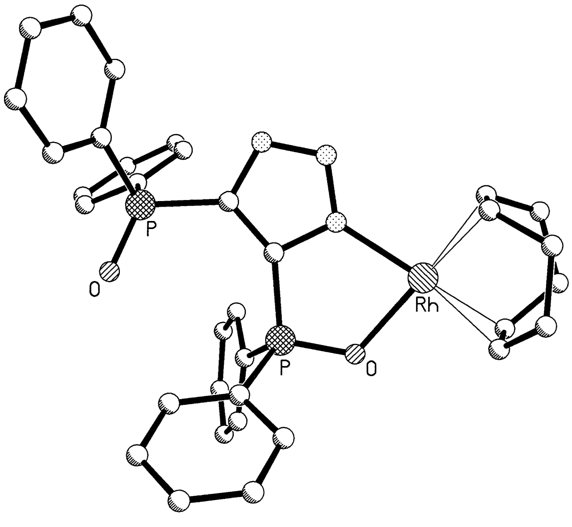


Figure 2. The structure of $[Rh(L^T)(cod)]$ (**2**).

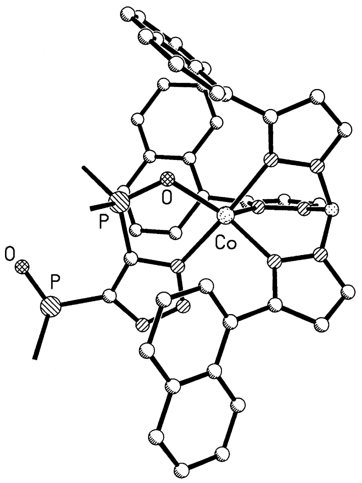


Figure 3. The structure of $[Co(L^T)(Tp^{\alpha Nt})]$ (**3**). The phenyl groups are not shown for the sake of clarity.

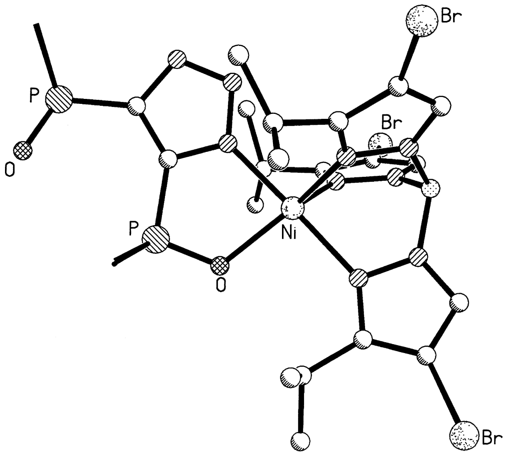


Figure 4. The structure of $[Ni(L^T)(Tp^{iPr,4Br})]$ (**4**). The phenyl groups are not shown for the sake of clarity.

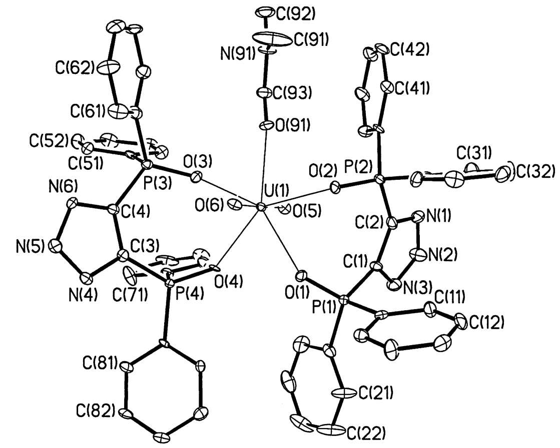


Figure 5. Molecular structure of $[UO_2(L^T)(dmf)] \cdot DMF$ (**5**) (30 % thermal ellipsoids). Selected bond lengths [Å] and angles [°]: U(1)-O(1) 2.380(6), U(1)-O(2) 2.372 (6), U(1)-O(3) 2.348(6), U(1)-O(4) 2.352(5), U(1)-O(5) 1.779(6), U(1)-O(6) 1.775(6), U(1)-O(91) 2.407(6); O(1)-U(1)-O(2) 71.6(2), O(3)-U(1)-O(4) 73.8(2), O(5)-(1)-O(6) 178.0(3), O(1)-U(1)-O(4) 71.2(2), O(2)-U(1)-O(3) 143.2(2).

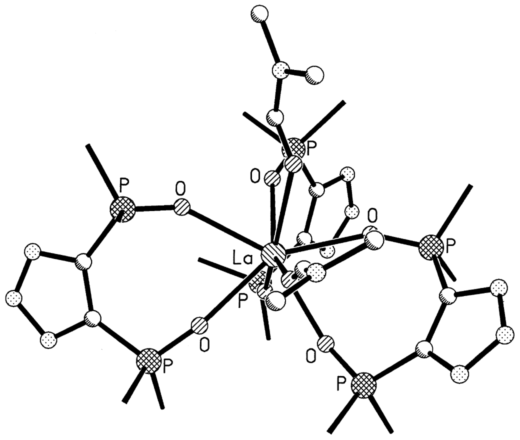


Figure 6. The structure of $[La(L^T)_3(dmf)_2]$ (**6**). The phenyl groups are not shown for the sake of clarity.

There was practically no difference in the triazolyl C–P bond lengths in the coordinated and the free $POPh_2$ substituents: they were all in a narrow 1.78–1.81 Å range. On the other hand, P–O bond lengths in the coordinated $POPh_2$ substituents were slightly longer than in the uncoordinated ones.

Anticipating that O,O-bonding might be achieved with more oxophilic metal ions, in spite of the sterically disfavored seven-membered ring, we synthesized the uranium complex, obtained as a DMF monosolvate, $[UO_2(L^T)_2(dmf)]$ (**5**; Figure 5), in which both L^T ligands were O,O-bonded, and the uranyl ion was in a pentagonal-bipyramidal seven-coordinate environment.

Further structurally characterized examples of L^T acting in κ^2 O,O-bonding fashion were also obtained. One such example was the lanthanum(III) complex $[La(L^T)_3]$ (**6;** Figure 6), which was recrystallized from DMF. In **6**, all three L^T ligands were O,O-coordinated, along with two additional O-bonded DMF molecules, placing La^{III} in an eight-coordinate environment. Another example was the O,O-chelated octahedral $[Mg(L^T)_3]^-$ ion **7**, obtained by the reaction of $MgSO_4$ with $[L^T][Et_3NH]$ in chloroform, even in the presence of excess $MgSO_4$. This anion was isolated and structurally characterized as the Et_3NH salt (Figure 7).

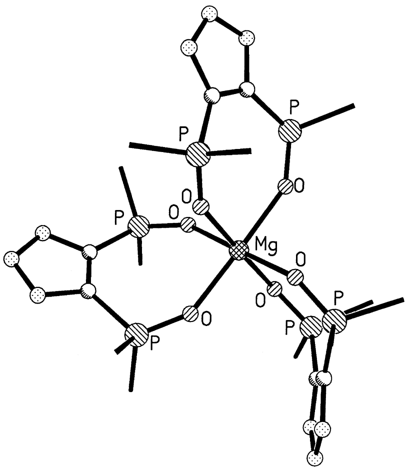


Figure 7. The structure of the anion $[Mg(L^T)_3]^-$ in $[Mg(L^T)_3][Et_3NH]$ (**7**). The phenyl groups are not shown for the sake of clarity.

The average U–O distances in $[UO_2(L^T)_2(dmf)]\cdot DMF$ (2.378 Å) were comparable to those in $[UO_2(acac)_2(H_2O)]$[8] and in $[UO_2(acac)_2(py)]$,[9] while the O-M-O angles were marginally larger than those in related acac complexes such as $[UO_2(acac)_2(py)]$[9] and $[UO_2(acac)_2(H_2O)]$.[8] In $[La(L^T)_3(dmf)_2]$ the average O-La-O angle was 71.5°, as compared with 68.5° in $[La(acac)_3(H_2O)_2]$.[10] Finally, the average O-Mg-O angles for $[Mg(L^T)_3]^-$ and $[Mg(acac)_2(H_2O)_2]$ were 90.0 and 82.7°, respectively; the very large difference is probably due to the steric crowding of twelve phenyl groups of the three coordinated L^T ligands around the small Mg^{2+} ion.[11]

Nucleophilic reactivity was demonstrated for the central nitrogen atom of L^T in the methylation reaction of the $[L^T]^-$ ion with methyl iodide, which yielded 2-methyl-4,5-bis(diphenylphosphinoyl)-1,2,3-triazole, as implied by its ^1H and ^{31}P NMR spectra which were indicative of C_{2v} symmetry. This neutral compound should be capable of the same reactions as the $[L^T]^-$ ion, except that the resulting complexes will be cationic. The relationship between $[L^T]^-$ and $[L^T]$-2-Me is reminiscent of that between $[HB(pz)_3]^-$ (=Tp; pz = pyrazolyl) and its neutral $HC(pz)_3$ analogue.

In summary, we have reported the synthesis of 4,5-bis(diphenylphosphinoyl)-1,2,3-triazole, L^TH, a powerful novel ligand which is the prototype of a new ligand class, and have demonstrated examples of its two different modes of coordination. This versatile chelating agent has potential not only as metal extractant or as a stable ligand core in diverse types of catalysis, but also as a possible model for N,PO, and $(PO)_2$ bonding modes for, for example, magnesium in biological systems. We are currently working at defining the boundaries for the different coordination modes of L^T as a function of the metal ion, and exploring the coordination chemistry of several variants of the L^T ligand system.

Experimental Section

Bis(diphenylphosphinoyl)acetylene was prepared by the literature method.[6] Satisfactory elemental analyses were obtained for all of the compounds mentioned below. NMR spectra were determined in $CDCl_3$.

L^TH: To a slurry of bis(diphenylphosphinoyl)acetylene (42.6 g) in methanol (200 mL) was added in one portion NaN_3 (7.0 g). The solid dissolved exothermally, yielding a solution of $Na[L^T]$, which could be used directly for the preparation of L^T complexes. This was done by mixing aliquot portions of the $Na[L^T]$ solutions with an aqueous solution of the appropriate metal perchlorate or nitrate salt. After dilution with a tenfold volume of water, the products were extracted with dichloromethane, passed through a short alumina column, and the eluate was evaporated. The free ligand L^TH was obtained by pouring the NaL^T solution into aqueous HCl, and purifying the filtered, water-washed, and dried precipitate by recrystallization from boiling DMF. M.p. 333–334 °C.

$[L^T][HNEt_3]$: To a slurry of L^TH in methanol was added excess triethylamine, and the resulting solution was evaporated to dryness. The residue was stirred with acetone and filtered. This yielded $[L^T][HNEt_3]$, which gradually darkened and decomposed from 330 °C. This salt is very soluble in dichloromethane and chloroform. ^1H NMR: $\delta = 7.69$ (m, 8H; Ph), 7.31 (m, 4H; Ph), 7.20 (m, 8H; Ph), 3.13 (quart., 6H; Et), 1.13 (t, 9H; Et); ^{31}P NMR: $\delta = 19.2$.

$[L^T]$-2-Me was prepared by adding a slight excess of MeI to a solution of $[L^T]Na$, and stirring the solution overnight. Addition of water and chloroform led to two phases, and the product was isolated from the organic phase. M.p. 210–211 °C. ^1H NMR: $\delta = 7.65$ (m, 8H; Ph), 7.44 (m, 4H; Ph), 7.29 (m, 8H; Ph), 4.17 (s, 3H; Me); ^{31}P NMR: $\delta = 18.68$.

Crystallographic data for $[Co(L^T)_2(py)_2]\cdot 2py$ (**1**) and $[UO_2(L^T)(dmf)]\cdot DMF$ (**5**) were collected on a Bruker P4/CCD diffractometer. For **1**: $C_{72}H_{60}CoN_{10}O_4P_4$, triclinic, $P\bar{1}$, $\phi_w = 1312.11$, $a = 10.37830(8)$, $b = 13.3831(2)$, $c = 13.5025(2)$ Å, $\alpha = 113.0332(9)$, $\beta = 98.0195(7)$, $\gamma = 97.1090(7)°$, $V = 1675.97(6)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.300\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 4.08\ cm^{-1}$, T(min/max) = 0.776, 0.998; 10866 data collected, 7059 independent, 412 parameters refined, $R(1) = 0.0482$ ($I = 2\sigma(I)$), $wR2 = 0.1042$, $T = 213(2)$ K. For **5**: $C_{58}H_{54}N_8O_8P_4U$, monoclinic, Pn, $\phi_w = 1353.00$, $a = 15.4055(1)$, $b = 10.6835(1)$, $c = 18.6390(2)$ Å, $\beta = 111.80(2)°$, $V = 2848.26(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.578\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 30.23\ cm^{-1}$, T(min/max) = 0.464, 0.864; 10302 data collected, 7054 independent, 712 parameters refined $R(1) = 0.0331$ ($I = 2\sigma(I)$), $wR2 = 0.0992$, $T = 193(2)$ K, absolute structure parameter = 0.023(6). Both samples were mounted on fine glass fibers. Compound **1** was found to be triclinic and the centrosymmetric alternative was initially chosen based on its greater frequency of occurrence. Compound **5** was found to be monoclinic; of the two space groups in agreement with the systematic absences, *Pn* and *P*2/*n*, the former was chosen due to a lack of rotational symmetry in the complex. Both choices were supported by the results of refinement which yielded narrow ranges for chemically related bond parameters. The data were corrected for absorption using SADABS.

Both structures were solved by direct methods and completed from subsequent difference maps. The asymmetric unit for **1** consists of one half of the Co complex residing on an inversion center and a molecule of pyridine, and for **5**, one U complex and a molecule of DMF. All non-hydrogen atoms were anisotropically refined and hydrogen atoms were placed in idealized locations. All software and sources of scattering factors were contained in the SHELXTL (5.1) library of programs (G. Sheldrick, Bruker-AXS, Madison, WI). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-143802 (**1**) and CCDC-143803 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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