Organometallics **1993,** *12,* 1503–1505

Transition-Metal Derivatives of the Cyclopentadienylphosphine Ligands. 8. Preparative Approaches and Characterization of the New Dinuclear Complex $[(\mu\text{-}C_5H_4P(C_6H_5)_2)Mo(CO)_2]_2$. X-ray Crystal Structure of the Tetrametallic Complex $[(CO)_3Mo(\mu\text{-}C_5H_4P(C_6H_5)_2)Ag]_2\cdot 2C_6H_5CH_3$

B. Brumas, D. de Caro, F. Dahan, D. de Montauzon, and R. Poilblanc*

Laboratoire de Chimie de Coordination du CNRS, Unité No. 8241 liée par conventions
à l'Université Paul Sabatier et à l'Institut National Polytechnique,
205 route de Narbonne, 31077 Toulouse Cedex, France

Received November 12, 1992

Summary: With the monometallic anionic complex $[(\eta^5\text{-}C_5H_4P(C_6H_5)_2)Mo(CO)_3]^-$ *(1), prepared in good yield from* $[(\eta^6\text{-}C_7H_8)Mo(CO)_3]$*, as starting material, three synthetic approaches toward the preparation of the homobimetallic doubly bridged derivatives* $[(\mu\text{-}C_5H_4P(C_6H_5)_2)Mo(CO)_2]_2$ *(3) have been investigated, namely an electro- and photochemical procedure, chemical oxidation by silver salt, and photodegradation of the hydride* $[(\eta^5\text{-}C_5H_4P(C_6H_5)_2)Mo(CO)_3H]$*. An intermediate in the second process, the tetrametallic complex* $[(CO)_3Mo(\mu\text{-}C_5H_4P(C_6H_5)_2Ag]_2$ *(4), has been isolated; its ring-shaped structure is characterized by normal Mo–Ag bonds and the absence of interaction between the two molybdenum atoms.*

Following our investigations on the synthesis and properties of new polymetallic complexes, we report here our first results on the synthesis of group 6 homobimetallic derivatives using the (diphenylphosphino)cyclopentadienide anion as bridging ligand. With the monometallic anionic complex $[(\eta^5\text{-}C_5H_4P(C_6H_5)_2)Mo(CO)_3]^-$ as starting material, three synthetic approaches implying basically oxidative reactions were investigated, namely (i) an electro- and photochemical procedure, (ii) chemical oxidation of the anion by silver tetrafluoroborate, and (iii) a photochemical preparation using the hydride $[(\eta^5\text{-}C_5H_4P(C_6H_5)_2)Mo(CO)_3)H]$. Interestingly, the second process leads to a novel tetrametallic Mo–Ag cyclic cluster.

Electro- and Photochemical Synthesis of $[(\mu\text{-}C_5H_4P(C_6H_5)_2)Mo(CO)_2]_2$ (3). It is well-known that the oxidation of the anions $[(\eta^5\text{-}C_5H_5)M(CO)_3]^-$ (M = Cr, Mo, W) leads to bimetallic metal–metal-bonded complexes,[1] and we have first investigated a synthetic pathway starting from the analogous monometallic anion $[(\eta^5\text{-}C_5H_4P(C_6H_5)_2)Mo(CO)_3]^-$ (1).

As reported by Casey et al., the preparation of this anion 1 from lithium (diphenylphosphino)cyclopentadienide and the hexacarbonyl complex $Mo(CO)_6$ is not straightforward, as the reaction simultaneously produces the pentacarbonyl anion $[(CO)_5MoP(C_6H_5)_2C_5H_4]^-$, which is impossible to separate from the expected product.[2] In order to get 1 in a pure form, we have used (cycloheptatriene)molybdenum tricarbonyl, $[(\eta^6\text{-}C_7H_8)Mo(CO)_3]$, as the starting material.[3] The compound was fully characterized by IR, ^1H NMR, and $^{31}P\{^1H\}$ NMR.[3] Its $^{31}P\{^1H\}$ NMR spectrum in C_6D_6 shows a unique singlet whose chemical shift at δ −18.2 is fully consistent with the absence of a phosphorus–molybdenum bond. Moreover, it shows in THF four infrared bands of vibration assigned to the C–O stretches at 1909 (vs), 1813 (vs), 1789 (s), and 1723 (s) cm^{-1}, in good accordance with the previous observations of Casey et al.[2] and quite close to the bands observed for the anionic parent compound $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]Li$ (1905, 1807, 1780, and 1714 cm^{-1} in THF).[2,4,5]

Attempting to reach the metal–metal-bonded complex $[(\eta^5\text{-}C_5H_4P(C_6H_5)_2)Mo(CO)_3]_2$ (2) (Scheme I), we have performed the oxidative electrolysis of 1 at 100 mV, on a platinum-gauze electrode in acetone with 0.1 M Et_4NBF_4 electrolyte.[6] The orange solution of 1 in acetone turned progressively dark red when one electron/mol of 1 was exchanged.[7] Although the infrared spectrum of the resulting solution appeared complicated, the two main bands, respectively at 1959 and 1913 cm^{-1} in THF, were attributable to 2 by comparison with the parent compound $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ (1960 and 1914 cm^{-1} in CCl_4). The formation of 2 was also confirmed by the $^{31}P\{^1H\}$ NMR

---

(1) Connelly, N. G.; Geiger, W. E. *Adv. Organomet. Chem.* **1984,** *23,* 1–93.

(2) Casey, C. P.; Bullock, R. M.; Fultz, W. C.; Rheingold, A. L. *Organometallics* **1982,** *1,* 1591–1596.

(3) Synthesis and characterization of $[(\eta^5\text{-}C_5H_4P(C_6H_5)_2)Mo(CO)_3]Li$: Addition of lithium (diphenylphosphino)cyclopentadienide to an equivalent amount of $[(\eta^6\text{-}C_7H_8)Mo(CO)_3]$ in THF at 70 °C leads readily to the formation of a yellow solution of 1, from which the corresponding lithium salt $[(\eta^5\text{-}C_5H_4P(C_6H_5)_2)Mo(CO)_3]Li$ is obtained as a beige powder in good yield (90%). ^1H NMR (200 MHz, C_6D_6): δ 7.70 and 7.46 (2 m, ortho), 7.14 (m, meta and para), 5.50 (br s, C_5H_4P). $^{31}P\{^1H\}$ NMR (80 MHz, C_6D_6): δ −18.2 (s). IR (THF, ν_{CO}): 1909 (vs), 1813 (vs), 1790 (s), 1724 (s) cm^{-1}.

(4) The occurrence of a fourth CO band instead of the three normally expected is attributed to the formation of a species in which an interaction occurs between the CO groups and the lithium cation. See: Darensbourg, M. Y. *Prog. Inorg. Chem.* **1985,** *33,* 221.

(5) The small increase of the infrared C–O stretching frequencies of 1 compared with those of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]^-$ could be tentatively attributed to some slippage of the cyclopentadienyl ring promoted by an orbital overlap between the $p\pi$ lone pair of the phosphorus atom and the π system of the C_5H_4P ring. See: (a) Lichtenberger, D. L.; Renshaw, S. K.; Basolo, F.; Cheong, M. *Organometallics* **1991,** *10,* 148–156. (b) Koller, M.; von Philipsborn, W. *Organometallics* **1992,** *11,* 467–469.

(6) An SCE was used as reference electrode, separated from the solution by a bridge compartment filled with the same solvent and supporting electrolyte solution as used in the cell. The counter electrode was a spiral of platinum wire of ca. 1 cm^2 apparent surface area. Anodic and cathodic compartments were separated by a porous medium frit. Electrochemical experiments were performed in an airtight cell connected to a vacuum/argon line.

(7) Noticeably, the number *n* of electrons exchanged per mole of 1 during the exhaustive electrolysis was limited to around n = 0.6 because of the silting of the frit. Therefore, we have used for purposes of electron counting an electrolytic cell without a frit.

0276-7333/93/2312-1503$04.00/0

Scheme I

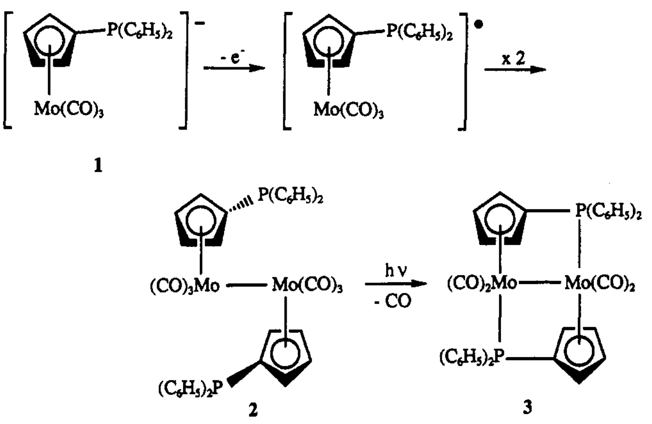
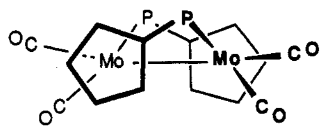


Chart I



spectrum in C_6D_6, which shows a singlet at δ −17.0 consistent with the presence of a dangling phosphine arm. A second species authenticated as $[(\mu\text{-}C_5H_4P(C_6H_5)_2)Mo(CO)_2]_2$ (**3**), according to its $^{31}P\{^1H\}$ NMR chemical shift, was also present in solution. Our aim was then to transform **2** into the expected bridged complex **3**, by means of a photochemical substitution process of a CO group by the uncoordinated extremity of the substituted η^5-bonded ligand. For this purpose, we have not struggled further to purify complex **2** and have only eliminated the supporting electrolyte through two cycles of evaporation to dryness and redissolution vs different solvents, from acetone to THF, in which Et_4NBF_4 is not soluble, and then from THF to toluene. This red toluene solution, containing **2** as the main product together with a small amount of **3**, spontaneously formed, was irradiated with a Hg low-pressure vapor lamp. The unique product **3** was effectively obtained and then isolated as a brown red powder (yield 50%) from which red crystals analyzed as $[(\mu\text{-}C_5H_4P(C_6H_5)_2)Mo(CO)_2]_2$ were obtained by slow diffusion of ether in the CH_2Cl_2 solution. The new compound was clearly identified by mass spectrometry[8] and in $^{31}P\{^1H\}$ NMR by a singlet at δ 68.2, characterizing a phosphorus atom directly bonded to molybdenum. The infrared spectrum of **3** shows four C–O stretching bands, suggesting a low symmetry of the molecule. This is confirmed by the ^1H NMR spectrum,[8] in which the four protons of the C_5H_4P groups appear at different shifts. As there is no obvious reason to consider that the two $[(\eta^5\text{-}C_5H_4P(C_6H_5)_2)Mo(CO)_2]$ moieties have different structures, this result shows that each of them does not admit a plane of symmetry. Comparing the CO stretching frequencies[8] of **3** with those of the closely related metal–metal-bonded bimetallic complex $[(\eta^5\text{-}C_5H_5)Mo(CO)_2P(C_6H_5)_3]_2$[9] (1850 (s), 1831 (vs) cm^{-1}) confirms the activity of the totally symmetrical mode (at 1941 cm^{-1}) and therefore the absence of a center of symmetry. Assuming a square-pyramidal coordination of each molybdenum atom as usually observed in related compounds, we propose for **3** the structure shown in Chart I, which fits the spectroscopic data.

Chemical Oxidation of the Anion $[(\eta^5\text{-}C_5H_4P(C_6H_5)_2)Mo(CO)_3]^-$ (1). Synthesis and Molecular Structure of $[(CO)_3Mo(\mu\text{-}C_5H_4P(C_6H_5)_2)Ag]_2$ (4). Considering the value of the oxidation potential of **1** (E_p = 100 mV), it was advisable to use the ferrocenium or silver cations as oxidizing reagents. In the first case, we were unable to get a clean reaction, suitable as a preparative procedure. In contrast, when 1 equiv of silver tetrafluoroborate as crystals was added to a toluene solution of **1** at room temperature, a gray precipitate of lithium fluoroborate appeared, which was easily separated.[10] From the resultant solution one can obtain in high yield (85%) yellow crystals of $[(CO)_3Mo(\mu\text{-}C_5H_4P(C_6H_5)_2)Ag]_2$ (**4**).

The complex **4** has been fully authenticated by elemental analysis, MS, and IR, ^1H NMR, ^{13}C NMR, and $^{31}P\{^1H\}$ NMR spectroscopy.[11] A crystal structure determination[12] reveals the presence of a discrete $[(CO)_3Mo(\mu\text{-}C_5H_4P(C_6H_5)_2)Ag]_2$ molecule and two molecules of toluene of crystallization per formula unit. Figure 1 shows the head-to-tail disposition of the bridging ligands, which is similar to that observed in many of the dimetallic derivatives of the same bridging unit.[13] The most significant feature is the bonding of the silver atom to the molybdenum center and its coordination by the phosphine which shapes the compound in the form of a cyclic cluster. Nevertheless, the conformation around the molybdenum atoms is not different from that observed in the various derivatives of the $(\eta^5\text{-}C_5H_5)Mo(CO)_2L$ fragment. The Mo–Mo distance (d_{Mo-Mo} = 6.7438(7) Å) is long enough to prevent any metal–metal interaction. The value of the angle Mo–Ag–P (168.57(3)°) leads us to describe the complex as a new example of near-linear, two-coordinated silver(I)–transi-

---

(8) Characterization of $[(\mu\text{-}C_5H_4P(C_6H_5)_2)Mo(CO)_2]_2$: ^1H NMR (200 MHz, C_6D_6) δ 7.90 and 7.75 (2 m, ortho), 7.13 (m, meta and para), 4.89 (s), 4.42 (s), 3.73 (s), 3.15 (s) (C_5H_4P); $^{31}P\{^1H\}$ NMR (80 MHz, C_6D_6) δ 68.2 (s); ^{13}C NMR (200 MHz, C_6D_6) δ 244.5 (d, $^1J_{CP}$ = 27 Hz, CO), 232.3 (s, CO), 140.4 (d, $^1J_{CP}$ = 41 Hz, ipso), 134.3 and 133.4 (2 s, para), 135.2 and 132.2 (2 d, $^1J_{CP}$ = 10 Hz, ortho), 131.6 and 130.7 (2 s, meta), 94.1 and 88.2 (2 s, C_3 of C_5H_4P), 91.8 and 88.6 (2 d, $^1J_{CP}$ = 11 Hz, C_2 of C_5H_4P), 53.6 (d, $^1J_{CP}$ = 41 Hz, C_1 of C_5H_4P); IR (THF, ν_{CO}) 1941 (s), 1896 (s), 1865 (w), 1843 (m); MS (DCI/NH_3) *m/e* 802 [MH^+] showing an isotopic pattern characteristic for a dimolybdenum compound. Anal. Calcd for $C_{38}H_{28}O_4P_2Mo_2$: C, 56.90; H, 3.52. Found: C, 57.20; H, 3.56.

(9) Bruce, M. I.; Goodall, B. L.; Sharrocks, D. N.; Stone, F. G. A. *J. Organomet. Chem.* **1972**, *39*, 139–143.

(10) Noticeably, the gray coloration of the precipitated lithium tetrafluoroborate was shown to be due to a small amount of metallic silver. This should not be associated with a possible decomposition of **4** toward the bimetallic complex **3** not observed at the end of the reaction (Scheme II) but with the occurrence of a presently unidentified side product.

(11) Characterization of $[(CO)_3Mo(\mu\text{-}C_5H_4P(C_6H_5)_2)Ag]_2$: ^1H NMR (200 MHz, C_6D_6) δ 7.69 (m, ortho), 7.15 (m, meta and para), 5.36 (quart, $^1J_{HP}$ = 2.3 Hz, α of P), 4.96 (quint, β of P); $^{31}P\{^1H\}$ NMR (200 MHz, C_6D_6) δ 6.3 (2 m), $^1J_{P-Ag}$ = 445 Hz; ^{13}C NMR (250 MHz, THF-d_8) δ 234.4 (s, CO), δ 134.8 (d, $^1J_{CP}$ = 16 Hz, ortho), 133.9 (d, $^1J_{CP}$ = 34 Hz, ipso), 132.4 (s, para), 130.5 (d, $^1J_{CP}$ = 11 Hz, meta), 95.1 (d, $^1J_{CP}$ = 42 Hz, C_1 of C_5H_4P), 93.6 (d, $^1J_{CP}$ = 14 Hz, C_2 of C_5H_4P), 92.7 (d, $^1J_{CP}$ = 7 Hz, C_3 of C_5H_4P); IR (CH_2Cl_2, ν_{CO}) 1941 (vs), 1857 (s), 1832 (vs) cm^{-1}; MS (DCI/NH_3) *m/e* 1074 [MH^+] showing the simulated isotopic pattern with a low intensity. The elemental analysis was performed on a sample at the terminal state of elimination of crystallization solvent. Anal. Calcd for $C_{40}H_{28}O_6P_2Mo_2Ag_2$: C, 44.72; H, 2.63. Found: C, 44.51; H, 2.74.

(12) Crystal data: $[(CO)_3Mo(\mu\text{-}C_5H_4P(C_6H_5)_2)Ag]_2\cdot 2C_6H_5CH_3$; a = 11.942(1) Å, b = 12.314(1) Å, c = 17.994(2) Å, β = 106.97(1)°, V = 2530.9(7) $Å^3$, monoclinic, space group $P2_1/c$, Z = 2. A total of 3094 intensity data were recorded in the ω–2θ scan mode on a CAD4 diffractometer using graphite-monochromatized MoKα radiation (λ = 0.710 73 Å). Full-matrix least-squares refinement with 2128 reflections having $F_0^2 > 2\sigma(F_o^2)$ led to final R values R = 0.022 and R_w = 0.024.

(13) He, X. D.; Maisonnat, A.; Dahan, F.; Poilblanc, R. *Organometallics* **1991**, *10*, 2443–2456.

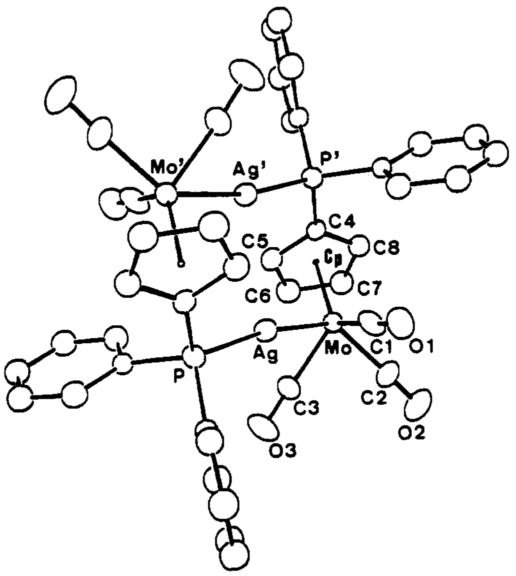


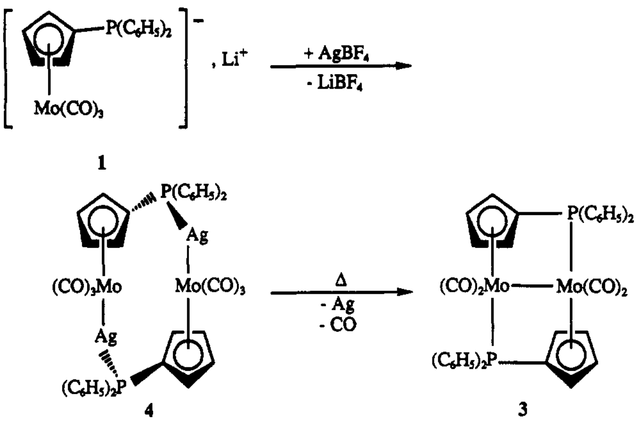
Figure 1. Ortep view of the cation for **4**. Selected bond distances (Å) and angles (deg) with esd's in parentheses include the following: Ag–Mo = 2.7467(4), Ag–P = 2.381(1), Mo–C(1) = 1.961(5), C(1)–O(1) = 1.183(6), Mo–C(cyclopentadienyl) = 2.355(9), P′–C(4) = 1.788(4); Mo–Ag–P = 168.57(3), Ag–Mo–Cp = 115.1(1) (Cp is the middle point of the cyclopentadienyl ring). The prime sign denotes centrosymmetric positions $1 - x, 1 - y, 1 - z$ (the atoms are represented by their 35% probability ellipsoids for thermal motion).

tion-metal compounds.[14] The Ag–Ag distance (3.1780(8) Å) is longer than those observed in Ag(I) complexes with certain sulfur ligands (2.96–3.09 Å,[14] compared to that measured in metallic Ag (2.87 Å)). Thus, it is difficult to attribute to an Ag–Ag interaction the apparent nearness of the Ag atoms and therefore the deviation from linearity of the angle Mo–Ag–P.

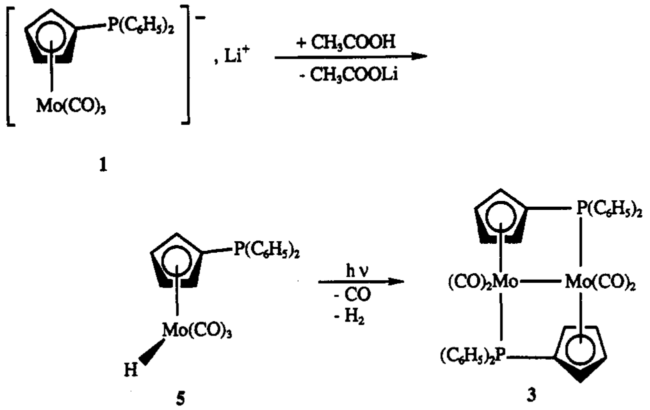
Thus, a toluene solution of **4** was heated at reflux, leading effectively to the formation of **3** (Scheme II). This reaction is not quantitative, and its byproducts were not identified. It is therefore not a convenient method for preparing **3**.

Photochemical Preparation of the Dimetallic Complex [(μ-$C_5H_4P(C_6H_5)_2$)$Mo(CO)_2$]$_2$ (3) Using the Hydrido Complex [(η^5-$C_5H_4P(C_6H_5)_2$)$Mo(CO)_3H$] (5) as Starting Material. The hydrido complex [(η^5-$C_5H_4P(C_6H_5)_2$)$Mo(CO)_3H$] (**5**) was readily prepared by adding 3 equiv of acetic acid to a toluene solution of [(η^5-$C_5H_4P(C_6H_5)_2$)$Mo(CO)_3$]Li (Scheme III). The yellow-orange solution instantaneously turned bright orange together with the formation of a light precipitate of lithium acetate. The hydrido complex **5** formed in solution was identified in $^{31}P\{^1H\}$ NMR by a singlet at δ −19.5, a chemical shift consistent with a dangling phosphino group, in ^1H NMR by a singlet at δ −5.26, and in infrared by two bands at 2024 (s) and 1937 (s, broad) cm^{-1} in toluene, in agreement with [(η^5-C_5H_5)$Mo(CO)_3H$] at 2029 and 1949–1945 cm^{-1}. The formation of a byproduct was also observed in $^{31}P\{^1H\}$ NMR at δ 59.37 in an approximate ratio of 1:6 with respect to **5**. This chemical shift value suggested the presence in this compound of a phosphorus–molybdenum bond.

Scheme II



Scheme III



To get the overall process shown in Scheme III, the above solution was irradiated with an Hg low-pressure lamp. Then, the resultant solution was shown by $^{31}P\{^1H\}$ NMR to contain only complex **3**. Therefore, the overall yield reaches 90% and this last procedure emerges as the most convenient of the three preparative approaches.[15]

Supplementary Material Available: Tables of fractional atomic coordinates, hydrogen atom positional and thermal parameters, final anisotropic thermal parameters, bond lengths and angles, interatomic distances, and least-squares planes (8 pages). Ordering information is given on any current masthead page.

OM9207166

---

[14] (a) Hackett, P.; Manning, A. R. *J. Chem. Soc., Chem. Commun.* **1973**, 71. (b) Connelly, N. G.; Lucy, A. R. *J. Chem. Soc., Chem. Commun.* **1981**, 43–44. See also: (c) Hackett, P.; Manning, A. R. *J. Chem. Soc., Dalton Trans.* **1974**, 1606–1609. (d) Kozitsyna, N. Y.; Ellern, A. M.; Struchkov, Y. T.; Moiseev, I. Y. *Mendeleev Commun.* **1992**, 100–102 and references therein.

[15] Three other synthetic procedures still with lower yields (less than 35%) have also been recently published by Mays, Conole, et al., during the revision of the present paper: Duckworth, J. J.; Mays, M. J.; Conole, G.; MacPartlin, M. J. *J. Organomet. Chem.* **1992**, *439*, 327–339.