Clearly more work needs to be done on the apparently more complex TACN system.

[9] a) P. Barbaro, C. Bianchini, K. Linn, C. Mealli, A. Meli, F. Vizza, *Inorg. Chim. Acta* **1992**, *198–200*, 31–56; b) S. Dutta, S.-M. Peng, S. Bhattacharya, *Inorg. Chem.* **2000**, *39*, 2231–2234.

[10] a) S. Han, L. D. Eltis, K. N. Timmis, S. W. Muchmore, J. T. Bolin, *Science* **1995**, *270*, 976–980; b) T. Senda, K. Sugiyama, H. Narita, T. Yamamoto, K. Kimbara, M. Fukuda, M. Sato, K. Yano, Y. Mitsui, *J. Mol. Biol.* **1996**, *255*, 735–752; c) A. Kita, S.-I. Kita, I. Fujisawa, K. Inaka, T. Ishida, K. Horiike, M. Nozaki, K. Miki, *Structure* **1999**, *7*, 25–34; d) K. Sugimoto, T. Senda, H. Aoshima, E. Masai, M. Fukuda, Y. Mitsui, *Structure* **1999**, *7*, 953–965.

[11] a) E. L. Hegg, L. Que, Jr., *Eur. J. Biochem.* **1997**, *250*, 625–629; b) L. Que, Jr., *Nature Struct. Biol.* **2000**, *7*, 182–185.

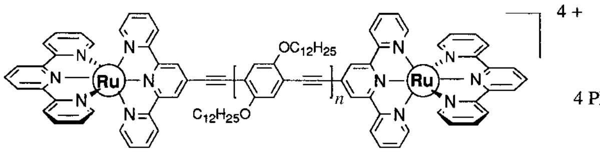
[12] K. Wieghardt, K. Pohl, W. Gebert, *Angew. Chem.* **1983**, *95*, 739–740; *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 727.

An Unusually Shallow Distance-Dependence for Triplet-Energy Transfer**

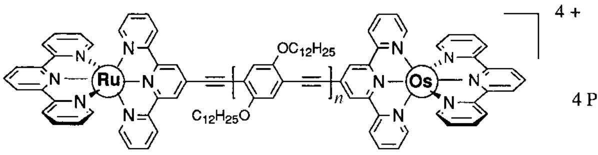
Anthony Harriman,* Abderrahim Khatyr, Raymond Ziessel,* and Andrew C. Benniston

There have been several reports of how the rate of intramolecular electron transfer[1] or triplet-energy transfer by electron exchange[2] decreases with increased separation of the reactants and, in many cases, an attenuation factor (β) describing an exponential drop-off has been noted. The attenuation factor, which is often better expressed in terms of the number of interspersed repeat units rather than distance,[3] has values ranging from around 0.05 to 1.7 Å^{-1} according to the nature of the connecting framework and the process under investigation.[4] It is recognized that the concept of an exponential-type attenuation factor applies only to those reactions that occur by way of superexchange[3] and, in other cases, the distance dependence might take on a different form.[5] With regard to triplet-energy transfer, this latter requisite demands that the transfer process involves electron exchange rather than dipole–dipole interactions. It is also important to ensure that the triplet energy of the interspersed connector unit does not fall below that of the donor triplet. This realization presents a particular problem with regard to the construction of long bridges from conjugated subunits where, as happens for polyacetylenes,[6] the triplet energy of the connector decreases with increasing length. In such cases, long-range triplet energy transfer will be replaced by sequential short-range steps that give a deceptively small β value.[7] Herein we report that superexchange-type behavior is retained over more than 50 Å when the polyacetylene is doped with phenylene groups. This system provides an unusually small attenuation factor for triplet energy transfer.[8, 9]

The required set of heterodinuclear complexes (Scheme 1), comprising ruthenium(II) and osmium(II) bis(2,2′:6′,2″-terpyridine) terminals separated by a 1,4-diethynylene-2,5-dialkoxybenzene connector, was prepared in a two-step procedure.



n = 1 **RR1**; n = 2 **RR2**; n = 3 **RR3**; n = 4 **RR4**; n = 5 **RR5**



n = 1 **RO1**; n = 2 **RO2**; n = 3 **RO3**; n = 4 **RO4**; n = 5 **RO5**

Scheme 1. The dinuclear $\mathrm{Ru^{II}}$-based complexes and the corresponding mixed-metal $\mathrm{Ru^{II}/Os^{II}}$ complexes.

First, the soluble polytopic ligands were treated with $[\mathrm{Ru(terpy)(dmso)Cl_2}]$[10] (terpy = 2,2′:6′,2″-terpyridine), dehalogenated with silver, in a mixture of dichloromethane and methanol to give the corresponding mono-$\mathrm{Ru^{II}}$ complexes in 54 to 81% yield. These complexes, which contain an uncoordinated terpy fragment, were subsequently treated with $[\mathrm{Os(terpy)(O)_2(OH)}](\mathrm{NO_3})\cdot 2\,\mathrm{H_2O}$ in aqueous tetrahydrofuran using excess hydrazine hydrate as reducing agent.[4] The resultant mixed-metal Ru/Os hybrids were precipitated as $\mathrm{PF_6}^-$ salts and purified by column chromatography on alumina prior to recrystallization from dichloromethane/hexane. Characterization was made by full spectroscopic and elemental analyses, including FAB$^+$ mass spectra which exhibited a molecular ion peak with the expected isotopic distributions and no significant peaks at higher mass. The corresponding dinuclear ruthenium(II) complexes were prepared according to a similar protocol using a slight excess of the metal precursor. Synthesis of the rationally designed polytopic ligands requires an iterative strategy based on palladium-promoted cross-coupling reactions to extend the central spacer framework outwards from the 1,4-diethynylene-2,5-diiododecyloxybenzene core.[11]

Photophysical properties for the dinuclear ruthenium(II) complexes were recorded in deoxygenated acetonitrile at 20°C following excitation at 532 nm. In particular, the luminescence maxima (λ_{MAX}), quantum yields (Φ_{LUM}), and lifetimes (τ_{LUM}) were as expected for an alkynylene-substi-

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tuted ruthenium(II) bis(terpyridine) complex;[12] such compounds are notably more emissive than the unsubstituted parent compounds. More importantly, the photophysical properties are quite insensitive to the length of the connecting unit (Table 1). This observation, taken together with the characteristic emission profile,[12] strongly supports the idea that the triplet state is localized on one of the terminal metal complexes. Even for the longest connector (**RR5**) there is no indication that the triplet state associated with the polytopic ligand is populated to any reasonable extent. Laser flash photolysis studies confirmed the impression that the lowest-energy triplet state involves the terminal units, not the connector, since the transient absorption spectra show clear bleaching of the metal-to-ligand, charge-transfer absorption band associated with the metal complex. As such, the triplet state of the connector must lie above that of the terminal metal complex ($E_T = 15230\ \text{cm}^{-1}$)[12] despite the apparent extended conjugation running along the molecular axis.

Table 1. Photophysical properties recorded for the various mixed-metal Ru/Os and dinuclear Ru^{II}-based complexes recorded in deoxygenated acetonitrile at 20 °C. Luminescence is from the Ru^{II}-based terminal ($\lambda_{EXCT} = 532$ nm) in the **RR** series but from the Os^{II}-based fragment ($\lambda_{EXCT} = 648$ nm) in the **RO** series.

n	Compound	λ_{LUM} [nm]	Φ_{LUM}	τ_{LUM} [ns]	Compound	λ_{LUM} [nm]	Φ_{LUM}	τ_{LUM} [ns]
1	**RR1**	693	0.0028	135	**RO1**	730	0.0086	165
2	**RR2**	695	0.0025	125	**RO2**	735	0.0075	140
3	**RR3**	692	0.0030	140	**RO3**	735	0.0085	160
4	**RR4**	694	0.0027	130	**RO4**	730	0.0088	160
5	**RR5**	695	0.0028	130	**RO5**	740	0.0080	155

Similar photophysical studies were made for the mixed-metal Ru/Os complexes in deoxygenated acetonitrile at 20 °C. Initially, the excitation wavelength was 648 nm, where only the Os^{II}-(terpy) chromophore absorbs incident photons. This allows the photophysical properties of the Os^{II}-based terminal to be determined (Table 1) and, again there is no obvious dependence on the nature of the connector. Excitation at 465 nm populates both Ru^{II}- and Os^{II}-based terminals, with the molar absorption coefficients slightly favoring the Ru^{II}-(terpy) complexes. Under these conditions, the luminescence spectra appear as mixtures of the two individual components that can be resolved by reference to the corresponding "pure" spectra recorded for the dinuclear Ru^{II} complexes and for the Os^{II} complexes using 648 nm excitation. This procedure allows estimation of the relative luminescence quantum yields for both terminals (Table 2) and it appears that emission from the Ru^{II}-based fragment becomes significantly less pronounced as the connector is shortened. Under identical conditions, emission from the corresponding Os^{II}-based unit increases, as would be expected if intramolecular triplet energy transfer occurs from the Ru^{II}-based unit to its Os^{II}-based counterpart.[13] The triplet energy gap, measured from the luminescence spectra,[12] is about 730 cm^{-1} and remains independent of separation distance.

These studies also indicate that luminescence around 650 nm is essentially that of the Ru^{II}-based terminal with only a minor contribution from the Os^{II}-based fragment.[12] Consequently, triplet lifetimes could be determined for the Ru^{II}-based terminals and compared with those recorded earlier for the dinuclear Ru^{II} complexes in order to estimate rate constants (k_{ET}) for intramolecular triplet-energy transfer in the mixed-metal systems (Table 2). The derived values are shown in Figure 1 in the form of their distance dependence (R), where distance refers to the computed average separation of the metal centers as determined by MM3 computer simulations. That intramolecular triplet-energy transfer occurs in these systems is confirmed by the observation that part of the emission associated with the Os^{II}-based terminal grows-in after the excitation pulse and on a time scale closely comparable to the decay of the Ru^{II}-based fragment. Furthermore, calculation of the rate of Förster-type dipole–dipole energy transfer[14] indicates that this process is unlikely to contribute more than a few percent to the overall reaction. Triplet-energy transfer, therefore, can be attributed to Dexter-type electron exchange[15] and, because of the constrained conformational mobility of these molecules, must involve long-range interactions.

Table 2. Parameters associated with intramolecular triplet-energy transfer in the mixed-metal Ru/Os dyads.

n	Compound	$\langle Ru\rangle$[a]	$\langle Os\rangle$[b]	k_{ET} [$10^7\ s^{-1}$]	R [Å]	V_{DA} [cm^{-1}]
1	**RO1**	0.01	1.92	11.6	19.8	0.90
2	**RO2**	0.26	1.78	3.2	27.9	0.46
3	**RO3**	0.40	1.55	1.3	36.0	0.29
4	**RO4**	0.52	1.40	0.77	44.1	0.22
5	**RO5**	0.79	1.15	0.22	52.3	0.12

[a] Relative luminescence yield for the Ru^{II}-based fragment calculated with respect to the corresponding dinuclear Ru^{II} complex and allowing for competitive light absorption by the appended Os^{II}-based unit. [b] Relative luminescence yield for the Os^{II}-based fragment calculated with respect to the measurement made with excitation at 648 nm and allowing for differences in the molar absorption coefficient at the respective excitation wavelengths.

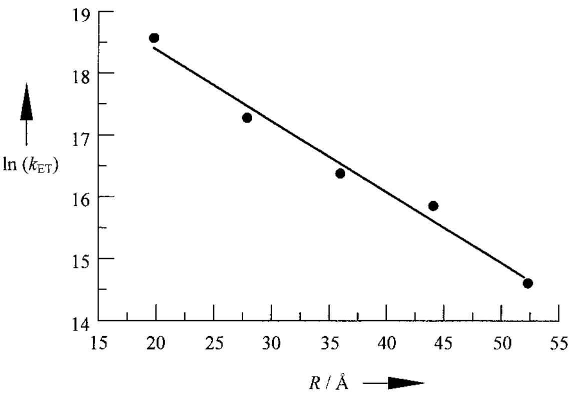

Figure 1. Effect of the metal–metal separation distance (R) on the rate constant (k_{ET}) for intramolecular electron exchange in the mixed-metal Ru/Os complexes.

The form of Figure 1 shows that the rate of intramolecular electron exchange decreases exponentially with increasing separation distance, at least up to around 52 Å, in accordance with [Eq. (1)]. Here, R refers to the metal–metal separation

$$k_{\mathrm{ET}} = A\exp(-\beta R) \qquad (1)$$

estimated from the energy-minimized conformation and provides an attenuation factor β of 0.11 ± 0.01 Å^{-1}. This is a remarkably small value[8, 9] that must arise from exceptionally good blending of molecular orbitals on adjacent units in the bridge, perhaps assisted by the radial distribution of the acetylenic groups. This β value implies that triplet energy transfer could be effected over a very long distance (i.e. >100 Å). The high solubility of the polytopic ligands and of the resultant metal complexes suggests that the synthesis of such long supermolecules is feasible. It is noteworthy that without the alkynylene substituent the triplet lifetime of the parent complex is too short to sustain energy transfer.[12] Each repeating unit in the connector adds about 8.1 Å to the metal–metal separation and causes a threefold drop in the rate of electron exchange. Regardless of how β is expressed it is clear that the extrapolated rate constant for electron exchange at orbital contact ($A \approx 10^9$ s^{-1}) is unusually small.[16] This suggests that the first bridging unit introduces a significant barrier to electron exchange but additional units have only a modest effect on the barrier height.

Indeed, the rate of electron exchange can be considered in terms of the Fermi golden rule[17] to estimate the magnitude of the electronic coupling matrix element (V_{DA}) for the process [Eq. (2)]. In this expression, FC is the Franck–Condon

$$k_{\mathrm{ET}} = \frac{2\pi}{\hbar}\langle V_{\mathrm{DA}}\rangle^2 FC \qquad (2)$$

weighted density of states and can be calculated from luminescence spectra recorded for the two terminals.[18] The average value is $FC = 1.3 \times 10^{-4}$ cm. Using this value it becomes possible to estimate V_{DA} for each member of the series (Table 2). This analysis highlights the rather small V_{DA} (0.9 cm^{-1}) found for the shortest bridge and confirms the restricted attenuation with increasing number of repeat units.

It is also surprising, at least at first sight, that the triplet state remains localized on either terminal without obvious population of the connector triplet. This must mean that the latter triplet lies at too high energy to be formed as a real intermediate but is able to mediate triplet-energy transfer by way of superexchange interactions. We suppose that the interspersed aromatic units disrupt electronic coupling along the molecular axis[19] and serve to raise the triplet energy of the connector. The alkoxy chains might further decouple the subunits because of local steric crowding and/or by forcing the phenylene rings into an unfavorable orientation. It is also important to note that, although the conformation is constrained, these molecules are far from rigid and might be expected to undergo substantial out-of-plane bending.[20] There has been some recent commentary[21] on how large-scale nuclear motion might be coupled to charge migration in DNA and it is possible that a similar process happens in these simple dyads.

Experimental Section

All new complexes were prepared by complexation of the back-to-back terpyridine ligands with the appropriate metal precursors and synthetic details will be reported elsewhere. Selected data are: **RO1** (52 %); FT-IR (KBr pellets): $\tilde{\nu} = 3428$ (m), 2922 (s), 2853 (s), 1730 (w), 1462 (m), 1260 (m), 1108 (m), 843 cm^{-1} (s); UV/Vis (CH_2Cl_2): $\lambda_{\max}$ [nm] (ε [M^{-1}cm^{-1}]); 273 (38,200), 281 (38,400), 309 (41,200), 487 (12,100); FAB$^+$ m/z 2151 ([$M - PF_6$]$^+$, 100); elemental analysis calcd (%) for $C_{94}H_{94}N_{12}O_2RuOsP_4F_{24}$: C 49.20, H 4.13, N 7.32; found: C 49.53, H 4.32, N 7.62. **RO2** (48 %); FT-IR (KBr pellets): $\tilde{\nu} = 3434$ (m), 2922 (s), 2851 (m), 1960 (m), 1636 (s), 1460 (m), 1258 (m), 1022 (m), 842 cm^{-1} (s); UV/Vis (CH_2Cl_2): $\lambda_{\max}$ [nm] (ε [M^{-1}cm^{-1}]); 275 (45000), 310 (40600), 490 (12900); FAB$^+$ 2619 ([$M - PF_6$]$^+$, 100); elemental analysis calcd (%) for $C_{126}H_{146}N_{12}O_4RuOsP_4F_{24}$: C 54.76, H 5.32, N 6.08; found: C 55.04, H 5.58, N 5.89. **RO3** (58 %); FT-IR (KBr pellets): $\tilde{\nu} = 3070$ (w), 2925 (s), 2853 (s), 2205 (w, C≡C), 1604 (s), 1504 (m), 1466 (s), 1430 (m), 1207 (s), 1030 (m), 843 cm^{-1} (s); UV/Vis (CH_2Cl_2): $\lambda_{\max}$ [nm] (ε [M^{-1}cm^{-1}]); 273 (27900), 309 (33200), 498 (13500); FAB$^+$ 3087 ([$M - PF_6$]$^+$, 100); elemental analysis calcd (%) for $C_{158}H_{198}N_{12}O_6RuOsP_4F_{24}$: C 58.71, H 6.17, N 5.20; found: C 58.43, H 5.92, N 5.01. **RO4** (65 %); FT-IR (KBr pellets): $\tilde{\nu} = 3429$ (s), 2927 (m), 2066 (m), 2001 (m), 1958 (s), 1748 (w), 1186 (s), 923 (s), 843 cm^{-1} (m); UV/Vis (CH_2Cl_2): $\lambda_{\max}$ [nm] (ε [M^{-1}cm^{-1}]); 274 (53200), 308 (55400), 485 (16100); FAB$^+$ 2410 ([$M - 2PF_6$]$^+$, 100); elemental analysis calcd (%) for $C_{190}H_{250}N_{12}O_8RuOsP_4F_{24}$: C 61.66, H 6.81, N 4.54; found: C 61.51, H 6.43, N4.28. **RO5** (66 %); FT-IR (KBr pellets): $\tilde{\nu} = 3434$ (s), 2920 (s), 2851 (m), 2199(w, C≡C), 1959 (m), 1633 (s), 1465 (s), 1443 (m), 841 (s), 765 cm^{-1} (s); UV/Vis (CH_2Cl_2): $\lambda_{\max}$ [nm] (ε [M^{-1}cm^{-1}]); 272 (17400), 309 (21800), 430 (14600), 498 (12900); elemental analysis calcd (%) for $C_{222}H_{302}N_{12}O_{10}RuOsP_4F_{24}$: C 63.94, H 7.30, N 4.03; found: C 63.62, H 7.12, N 3.93.

Photophysical measurements were made in deoxygenated acetonitrile at 20 °C using conventional methods. Luminescence lifetimes were measured after excitation with a 25 ps laser pulse delivered from a frequency-doubled Nd-YAG laser equipped with a Raman shifter. The temporal resolution of this instrument is approximately 200 ps. Separation distances were calculated from energy-minimized conformations using the TITAN software.

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[1] A. Harriman, *R.S.C. Specialist Periodical Reports Photochemistry*, **1999**, *29*, chap. 1 and 7.

[2] a) G. L. Closs, P. Piotrowiak, J. M. MacInnis, G. R. Fleming, *J. Am. Chem. Soc.* **1988**, *110*, 2652; b) H. Oevering, J. Verhoeven, N. M. Paddon-Row, E. Cotsaris, N. S. Hush, *Chem. Phys. Lett.* **1988**, *143*, 488; c) F. Barigelletti, L. Flamigni, *Chem. Soc. Rev.* **2000**, *29*, 1.

[3] G. L. Closs, J. R. Miller, *Science* **1988**, *240*, 440.

[4] V. Grosshenny, A. Harriman, R. Ziessel, *Angew. Chem.* **1995**, *107*, 1211; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1100.

[5] A. K. Felts, W. T. Pollard, R. A. Freisner, *J. Phys. Chem.* **1995**, *99*, 2929.

[6] R. Ziessel, M. Hissler, A. El-ghayoury, A. Harriman, *Coord. Chem. Rev.* **1998**, *178–180*, 1251.

[7] A. El-ghayoury, A. Harriman, A. Khatyr, R. Ziessel, *Angew. Chem.* **2000**, *112*, 191; *Angew. Chem. Int. Ed.* **2000**, *39*, 185.

[8] The size of the attenuation factor (β) for intramolecular triplet energy transfer occurring by electron exchange depends on the nature of the connecting framework and the following values have been reported: $\beta = 0.17$ Å^{-1} for polyalkynes;[4] $\beta = 1.7$ Å^{-1} for DNA;[9a] $\beta = 1.33$ Å^{-1} for saturated hydrocarbons;[2b] $\beta = 0.32$[9b] or 0.64[9c] Å^{-1} for polyphenyls; $\beta = 1.7$ Å^{-1} for steroids.[2a]

[9] a) A. M. Brun, A. Harriman, *J. Am. Chem. Soc.* **1994**, *116*, 10383; b) B. Schlicke, P. Belser, L. De Cola, E. Sabbioni, V. Balzani, *J. Am. Chem. Soc.* **1999**, *121*, 4207; c) F. Barigelletti, L. Flamigni, M. Guardigli, A. Juris, M. Beley, S. Chadorowsky-Kimmer, J. P. Collin, J. P. Sauvage, *Inorg. Chem.* **1996**, *35*, 136.

[10] V. Grosshenny, R. Ziessel, *J. Organomet. Chem.* **1993**, *453*, 19.

[11] A. Khatyr, R. Ziessel, *Tetrahedron Lett.* **1999**, *40*, 5515.

[12] A. El-ghayoury, A. Harriman, A. Khatyr, R. Ziessel, *J. Phys. Chem. A* **2000**, *104*, 1512.

[13] P. F. H. Scwab, M. D. Lewin, J. Michl, *Chem. Rev.* **1999**, *99*, 1863.

[14] T. Förster, *Discuss. Faraday Soc.* **1959**, *27*, 7.

[15] D. L. Dexter, *J. Chem. Phys.* **1953**, *21*, 836.

[16] Typical pre-exponential factors (*A*) for electron exchange lie in the region of 10^{13} s^{-1} (see ref [3]) and should not be significantly affected by changes in temperature, chemical structure, or solvent polarity.

[17] a) M. Lax, *J. Chem. Phys.* **1952**, *20*, 1752; b) R. Kubo, Y. Toyozawa, *Prog. Theor. Phys.* **1955**, 160.

[18] Z. Murtaza, D. K. Graff, A. P. Zipp, L. A. Worl, W. E. Jones, Jr, W. D. Bates, T. J. Meyer, *J. Phys. Chem.* **1994**, *98*, 10504.

[19] M. P. Samanta, W. Tian, S. Dutta, J. I. Henderson, C. P. Kubiak, *Phys. Rev. B* **1996**, *53*, 7626.

[20] A. A. Bothner-By, J. Dadok, T. E. Johnson, J. S. Lindsey, *J. Phys. Chem.* **1996**, *100*, 17551.

[21] a) P. T. Henderson, D. Jones, G. Hampikian, Y. Kan, G. B. Schuster, *Proc. Natl. Acad. Sci. USA* **1999**, *96*, 8353; b) J. Jortner, M. Bixon, T. Langenbacher, M. E. Michel-Beyerle, *Proc. Natl. Acad. Sci. USA* **1998**, *95*, 12759; c) M. Ratner, *Nature* **1999**, *397*, 480.

The Distinct Effect of the *o*-Carboranyl Fragment: Its Influence on the I–I Distance in R_3PI_2 Complexes[**]

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Reijo Sillanpää, and Raikko Kivekäs

Although compounds of stoichiometry R_3PX_2 (R = organic substituent, X = halogen) have been known for over 100 years, their solid-state structure remains largely unexplored. This is surprising considering that some of these species have found significant use as reagents in synthetic organic and inorganic chemistry and are commercially available.[1] Interest in their solid-state structure has increased in the last decade since the structure of *t*Bu_3PI_2 was disclosed.[2] The existence of significant iodine–iodine interaction in this compound and the four-coordinate molecular structure, novel in phosphane chemistry, stimulated the interest of researchers in the area.[3, 4] Du Mont et al.[2] upon the observation that the I–I bond in *t*Bu_3PI_2 (3.326(1) Å) was longer than in Ph_3AsI_2 (3.005(1) Å),[5] suggested that it could be interpreted either as an iodophosphonium salt or as an iodine charge-transfer complex. With the incorporation of new data it was later considered as a charge-transfer complex.[6] The interpretation of the I–I interaction in R_3PI_2 molecules is, however, still a point of controversy as has been stated recently.[7] We shall consider the I$\cdots$I Van der Waals distance to be 4.3 Å, thus any distance smaller than this suggests an I–I bond interaction.

The structures of halophosphoranes in the solid-state depend largely on the starting phosphane R_nPX_{3-n}, the solvent used, the halogen, and the phosphane : halogen ratio.[8] In the solid-state structures of R_3PX_2 three basic structural motifs are found: trigonal bipyramidal in Ph_3PF_2,[9] $(C_6F_5)_3PCl_2$, $Ph_2(C_6F_5)PCl_2$,[10] and Ph_3PCl_2;[11] the molecular charge-transfer "spoke" structure for *t*Bu_3PI_2,[2] Ph_3PI_2,[3a] $PhMe_2PI_2$,[3b] Ph_3PBr_2,[12] *i*Pr_3PI_2[13] and Ph_3PIBr,[14] and the ionic form, for example, in [*n*Pr_3PCl]Cl,[10] and [Ph_3PCl]Cl.[4a] In the last two types of structure the P center is tetracoordinate. For this coordination, the distinction between molecular charge-transfer "spoke" structure and the ionic form is very tenuous, and there seems to be a continuum in the X–X bond strength. If attention is focused solely on R_3PI_2 compounds, a few examples exist which bring information on the I–I and P–I distances: in $PhMe_2PI_2$,[3b] *i*Pr_3PI_2,[13] *t*Bu_3PI_2[2] and Ph_3PI_2,[3a] the observed I–I bond lengths [Å], P–I bond lengths are in parenthesis, are 3.408(2) [2.410(2)], 3.383(1) [2.409(2)] and 3.372(1) [2.420(2)], 3.326(2) [2.461(2)], and 3.161(2) [2.481(4)], respectively. The shortening of the I–I bond implies that elongation of the P–I bond takes place. In no case has an I–I bond been found that is as short as that in Ph_3AsI_2 (3.005(1) Å).[5] For comparison, the I–I bond in I_2 is 2.660 Å.[15] The elongation of the I–I bond is expected since electron density is transferred into the σ^* orbital of the diiodine by the electron donor. As a consequence the more basic the phosphanes are the longer the I–I bond will be and thus the shorter the P–I bond.

The *o*-carborane, 1,2-$C_2B_{10}H_{12}$, is an icosahedral cluster in which the two carbon atoms are in adjacent positions. One way to build the orbital set of *o*-carborane is to consider that each participating atom has as its valence orbital set two sp, and two p orbitals. This situation is very similar to the molecular orbitals in acetylene. Consequently, the C–H group of *o*-carborane is acidic and may be removed by strong bases. Moreover, the *o*-carborane cage through substitution at carbon is extremely electron-withdrawing. During our research on *o*-carboranylmonophosphane derivatives, 1-PR_2-2-R′-1,2-$C_2B_{10}H_{10}$[16] (Figure 1), we considered the possibility that a molecular charge-transfer "spoke" structure could be obtained. This would provide data on the electron-withdrawing capacity of the *o*-carboranyl cluster through the influence on the I–I distance, and also allow new data concerning the R_3P-I-I continuum to be obtained. There are several *o*-carboranylmonophosphanes of the type (*o*-carboranyl)R_2P available, but we decided to look for one with the highest basicity. The R′ radical in 1-PR_2-2-R′-1,2-$C_2B_{10}H_{10}$ can be varied and although its influence on the basicity is not considerable it is adequate to improve crystallization; the R radicals influence on the phosphorous center is important. Thus, a basic carboranylphosphane was chosen to compensate for the −I (inductive effect) influence of the *o*-carboranyl cluster on the phosphorus center.

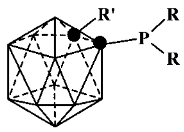

Figure 1. *closo*-Carboraylmonophosphane (● = C, other vertices are BH).

First assays with 1-P*i*Pr_2-2-Me-1,2-$C_2B_{10}H_{10}$ (**1**) were titrations with I_2 in dry $CHCl_3$. This has been a standard experiment in the development of this R_3PI_2 chemistry, and

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