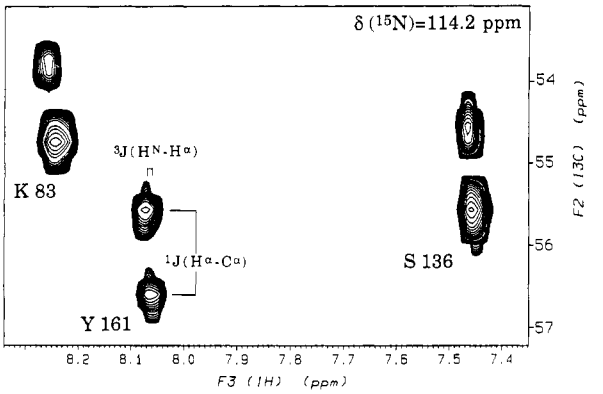

Figure 2. Expansion of an ω_2-ω_3 cross plane of a 3D spectrum recorded with the sequence of Figure 1 on uniformly (>95%) ^{13}C-^{15}N enriched T4 lysozyme at 25 °C. The protein, prepared as described previously,[16] was 4.3 mM in 100 mM KCl, 30 mM potassium phosphate, 5% D_2O, pH 5.5. The cross plane shown is at the ^{15}N frequency of 114.2 ppm containing the C^α-H^N cross peaks of Lys 83, Tyr 161, and Ser 136. The cross peaks are split in doublets along ω_2 with the one-bond H^α-C^α coupling of ~130 Hz. In addition, the two doublet components are displaced along ω_3 with the vicinal H^α-H^N coupling constant. These can readily be measured as 9.0, 5.0, and 4.5 ± 0.5 Hz from the peak positions of the two components. The spectrum was recorded on a Bruker AMX-600 spectrometer equipped with two external synthesizers and amplifiers. The GARP[13] decoupling of the carbonyls was achieved with a GARP box purchased from Tschudin Associates using a 90° pulse length of 400 μs. GARP decoupling of the nitrogens during detection was achieved with the internal nitrogen channel using 90° pulses of 150 μs. The 3D data set consisted of 32, 128, and 512 complex data points in t_1, t_2, and t_3, respectively. The data were zero-filled and truncated after Fourier transformation so that the final digital resolution was 21.7, 30.5, and 2.4 Hz in ω_1, ω_2, and ω_3, respectively. Chemical shifts are quoted relative to sodium 3-(trimethylsilyl)-(2,2,3,3-$^2H_4$)propionate (^1H and ^{13}C) and ammonia (^{15}N).

In addition, the two doublet components are displaced along ω_3 with the vicinal H^α-H^N coupling constant. This can readily be measured from the peak positions of the two components. Furthermore, the two components are split along the carbon axis due to the C^α-C^β coupling (30–35 Hz). This is not resolved in Figure 2 due to the low digital resolution along ω_2. Figure 2 shows a small part of an ω_2-ω_3 plane at a nitrogen frequency of 114.2 ppm containing the cross peaks for Lys 83, Tyr 161, and Ser 136 (^1H and ^{15}N assignments of this protein have been published previously,[15] and the assignment of the α-carbon resonances is trivial from this spectrum). The large doublet splitting of ~130 Hz along ω_2 and the displacement of the multiplet components along ω_3 can readily be seen. The H^N-H^α vicinal coupling constants measured are 9.0, 5.0, and 4.5 Hz, respectively. Currently, we are examining the best way to measure the coupling constants, such as separation of peak maxima, centers of mass, fit of line shapes, and the influence of the digital resolution on the precision of the measurements. It is worth mentioning that we can measure all H^N-H^α vicinal coupling constants in T4 lysozyme using this technique. A complete analysis of the coupling constants as well as a comparison with values expected from the X-ray structure is in progress and will be presented elsewhere. The measured values of the coupling constants are significantly smaller than the approximate 15-Hz line widths of the amide resonances and would be difficult to accurately measure using previous approaches.

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Polyether Tethered Oligonucleotide Probes

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Molecules capable of sequence-specific recognition of DNA[1] and RNA[2] have widespread utility in the biotechnology industry and as tools for the study of nucleic acid structure and function. Recognition of RNA is particularly challenging due to its increased potential for structural complexity[3] and the absence of three-dimensional structural data for most molecules.[4] Interestingly, the few well-characterized cases[5] suggest that, in terms of molecular architecture, RNA is related more closely to a globular protein than to duplex DNA.[4]

Recently we described a family of synthetic molecules for the sequence- and structure-specific recognition of RNA.[6] Tethered oligonucleotide probes (TOPs) consist of two deoxyoligonucleotides separated by a flexible, synthetic tether (Figure 1). The two oligonucleotides hybridize to two noncontiguous, single-stranded regions of a target RNA, and the tether traverses the distance between them (Figure 1).[7] When the tether is constructed from a repeating abasic phosphodiester unit that resembles DNA (as in **1** and **2**), TOPs bind cooperatively, monomerically, and with high affinity to two regions (labeled 3′- and 5′-site in Figure 1) of the *Leptomonas collosoma* SL RNA.[8] We questioned whether

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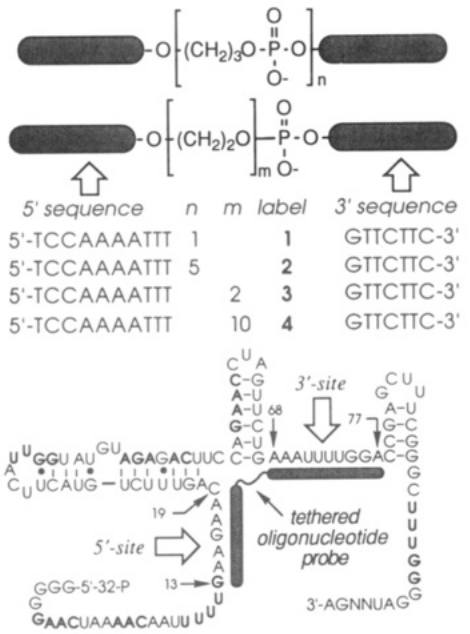

Figure 1. (Top) Structures of TOPs **1–4** and (bottom) the SL RNA–TOP complex. Bold type residues indicate sites partially complementary to TOPs **1–4**.

a tether that did not resemble DNA could bind as avidly. We now report that TOPs containing neutral poly(ethylene glycol) tethers (PEG-TOPs **3** and **4**)[9–11] are as effective as their phosphodiester counterparts for the recognition of RNA and therefore have potential as RNA-directed pharmaceuticals,[12] tools for the differentiation of RNA tertiary structures,[2] and reagents for the detection of RNA–RNA interactions.

The sequence specificity of TOPs **3** and **4** for the SL RNA was assayed by use of RNase H. Because it hydrolyzes the RNA strand of a RNA–DNA hybrid,[13–15] incubation of this enzyme with end labeled SL RNA and a TOP permits the TOP binding sites to be determined precisely when the reaction products are subjected to electrophoresis and autoradiography.[6] Cleavage patterns for **3** and **4** (Figure 2, lanes 4 and 8) indicate that binding occurs only at the targeted sites (G_{13}–C_{19} and A_{68}–A_{77}). Although several regions of the SL RNA exhibit partial complementarity to TOPs **3** and **4** (U_9–G_{13}, U_{35}–G_{38}, U_{93}–G_{96}; C_{-2}–G_{-5}, A_3–C_5, A_{44}–A_{46}, A_{54}–C_{58}), no cleavage is observed at these sites when the SL RNA is in excess.[16]

To determine if the two oligonucleotide sequences contained within **3** and **4** bind cooperatively to the SL RNA, and if 1:1 complexes are formed, we performed the following experiment (Figure 2). The oligoribonucleotide UCCAAAAUUU (**5**) complements RNA bases 68–77 and will therefore compete with TOPs **3** and **4** for the SL RNA. But **5** does not elicit RNase H cleavage of the SL RNA because the RNA–RNA hybrids formed are not RNase H substrates. Therefore, if TOPs **3** and **4** bind cooperatively to a single SL RNA molecule, and if the concentration of **5** is high enough to displace the TOP from the 3′-site at equilibrium, then the TOP should dissociate from the 5′-site as well,

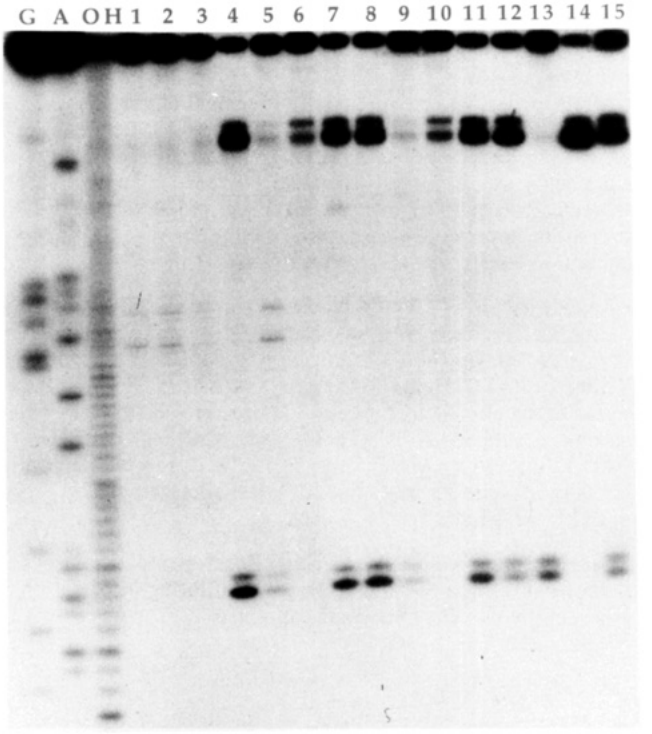

Figure 2. Autoradiogram of a 15% denaturing polyacrylamide gel illustrating recognition of the SL RNA by TOPs **3** and **4**. Lanes labeled A, G, and OH represent enzymatic (A, G) and alkaline (OH^-) sequencing lanes. Unless otherwise indicated, all reactions contained 0.72 μM SL RNA, <0.07 μM 5′-^{32}P-end-labeled SL RNA, 57.3 mM Tris-HCl, pH 8.1, 14 mM $MgCl_2$, 1.6 mM DTT, 67 mM KCl, 1.4 mM EDTA, 0.6 μg of BSA, between 2 and 10 units of RNAsin, 1.2 units of RNase H, and 5% glycerol. Lane 1, intact SL RNA (no RNase H, no probe); lane 2, 7.5 μM **3** (no RNase H); lane 3, RNase H control; lane 4, 75 nM **3**; lane 5, 75 nM **3**, 2.2 μM **5**; lane 6, 75 nM **3**, 37 μM **7**; lane 7, 75 nM **3**, 7.5 μM **6**; lane 8, 75 nM **4**; lane 9, 75 nM **4**, 2.2 μM **5**; lane 10, 75 nM **4**, 37 μM **7**; lane 11, 75 nM **4**, 7.5 μM **6**; lane 12, 75 nM **8**, 75 nM **9**, lane 13, 75 nM **8**, 75 nM **9**, 2.2 μM **5**; lane 14, 75 nM **8**, 75 nM **9**, 37 μM **7**; lane 15, 75 nM **8**, 75 nM **9**, 7.5 μM **6**. Procedures were as described.[6]

with a concomitant loss of RNase H sensitivity at bases 13–19. If the interaction between the TOP and the RNA is noncooperative or nonmonomeric, the TOP should remain bound to the 5′-site and be detected by RNase H cleavage. End-labeled[17] SL RNA was incubated with **3** or **4**, RNase H, and a 30-fold excess of **5**. In both cases, competition with **5** diminishes significantly the amount of RNA cleavage at both the 3′- and 5′-sites (compare lanes 4 and 5, and 8 and 9), while a 100-fold excess of a noncomplementary oligoribonucleotide [UCGGGCUUUGGG (**6**)] has no effect (lanes 7 and 11). The experiment can be performed in reverse with the identical result: an oligoribonucleotide including a sequence complementary to the 5′-site [GUUCUUCAAAAA (**7**)] is capable of reducing the 3′- and 5′-site cleavage elicited by RNase H and **3** or **4** (lanes 6 and 10). When deoxyoligonucleotides TCCAAAATTT (**8**) and GTTCTTC (**9**) are mixed together and incubated with the SL RNA and RNase H, competition with **5** fails to reduce cleavage at the 5′-site (compare lanes 12 and 13), and competition with **7** fails to reduce cleavage at the 3′-site (compare lanes 12 and 14). These results indicate a monomeric and cooperative binding motif for PEG-TOPs **3** and **4**.

In order to compare the poly(ethylene glycol) and polyphosphodiester TOPs, we determined the equilibrium dissociation constants of their SL RNA complexes using an electrophoretic mobility shift assay.[18] At 25 °C, we measured[19] a K_d of 88 ±

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6 nM for **3**, which equals almost exactly the K_d measured for **1**, 99 ± 6 nM. The K_d increases with tether length for both classes of probes: K_d(**4**) = 276 ± 12 nM, K_d(**2**) = 263 ± 8 nM. All tethered probes bind significantly better than oligonucleotides **8** and **9** [K_d(**8**) = 17 500 ± 2200 nM, K_d(**9**) = 135 000 ± 19 000 nM]. Therefore, two oligonucleotides united by a neutral tether designed to minimize electrostatic effects[20] recognize RNA molecules on the basis of *both* sequence and structure. This observation is very intriguing, since it suggests that TOPs could function as *molecular rulers for RNA*.

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Supplementary Material Available: Experimental details of the syntheses of probes **3** and **4** (5 pages). Ordering information is given on any current masthead page.

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Tris(phenylimido) Complexes of Tungsten: Preparation and Properties of the d^0 W(=NR)$_3$ Functional Group

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Despite their notoriety as inert ligands, highly reactive *early*-transition-metal imido[1] moieties (M=NR) may be generated—even toward C-H activation[2,3]—if sufficient electron density resides on the imido nitrogen.[3] One potential means to achieve this condition is to lade the metal center with strong π-donor ligands and thereby induce a competition for available d{π}-p{π} interactions.[2-4] Such "π-loading" may result from environments that employ *multiple imido* coordination, i.e., additional $[NR]^{2-}$ groups as the ancillary π-donors.[5] Established imido functional groups of d^0 tungsten include W=NR,[6] W(=NR)$_2$,[7] and [W(=NR)$_4^{2-}$],[8] but the tris(imido) complexes are conspicuously absent from this series. Herein, we report the preparation of the d^0 W(=NR)$_3$ functional group and demonstrate an electronic and structural analogy to related M(π-donor)$_3$ complexes.

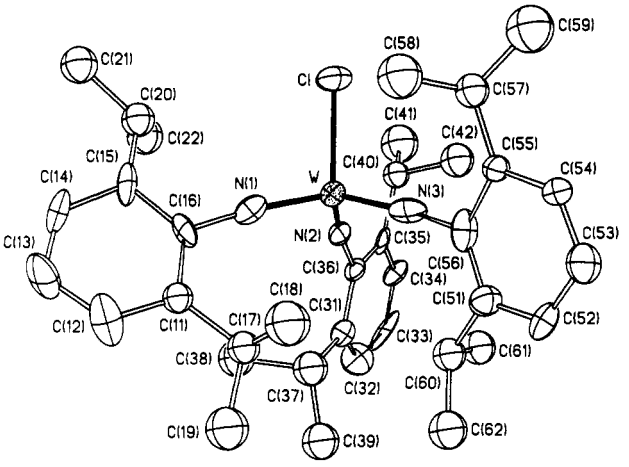

Figure 1. Molecular structure of the $[W(NAr)_3Cl]^-$ anion in $[Li(THF)_4][W(NAr)_3Cl]$ (**3**, Ar = 2,6-diisopropylphenyl) with atoms shown as 50% probability ellipsoids.

Upon reaction of W(NAr)Cl$_4$(THF)[9] with 2 equiv of $Me_3SiNHAr$ in THF (45 °C, 24 h, Ar = 2,6-diisopropylphenyl), red orange W(NAr)$_2$Cl$_2$(THF)$_2$ (**1**) forms in 87% yield. NMR data for **1** reveal[10] equivalent imido and THF ligands, thus a structure parallel to reported W(NR)$_2$Cl$_2$(L-L) chelate adducts is proposed (Scheme I).[7c,9,11] W(NAr)$_2$Cl$_2$(THF)$_2$ (**1**) is readily functionalized by using excess Me_3SiNEt_2 (in Et_2O) to provide orange crystals of W(NAr)$_2$(NEt$_2$)Cl (**2**). Upon reaction of W(NAr)$_2$Cl$_2$(THF)$_2$ (**1**) with 2 equiv of LiNHAr in THF (room temperature, 12 h), yellow crystalline **3** is obtained in high yield. The absence of a ν(N-H) mode in the IR spectrum of **3**, the lack of N*H* resonances in its ^{1}H NMR spectrum, its elemental analysis, and its reactivity (vide infra) all support the formulation of **3** as the tris(imido) complex $[Li(THF)_4][W(NAr)_3Cl]$.[12]

The structure of the $[W(NAr)_3Cl]^-$ anion in $[Li(THF)_4][W(NAr)_3Cl]$ (**3**, Figure 1)[13,14] reveals that the tungsten atom is

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(12) $[Li(THF)_4][W(NAr)_3Cl]$ (**3**): ^{1}H NMR (CD_2Cl_2) δ 6.97-6.65 (A_2B mult, 9 H, H_{aryl}), 3.71 (m, 16 H, $C_\alpha H$, THF), 3.57 (spt, 6 H, $CHMe_2$), 1.90 (m, 16 H, $C_\beta H$, THF), 1.06 (d, 36 H, $CHMe_2$); ^{13}C NMR (CD_2Cl_2) δ 140.4 (C_o), 125.1 (C_{ipso}), 122.0 (overlapping C_m and C_p), 68.7 (C_α, THF), 28.3 ($CHMe_2$), 25.8 (C_β, THF), 23.8 ($CHMe_2$). Anal. Calcd for $C_{52}H_{83}ClLiN_3O_4W$: C, 60.03; H, 8.04; N, 4.04; Cl, 3.41. Found: C, 59.54; H, 8.44; N, 4.15, Cl, 2.81.

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